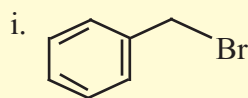


## 10. HALOGEN DERIVATIVES

### Can you recall ?

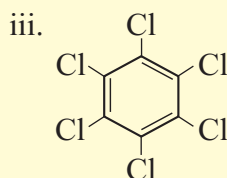
Identify the functional group in the following compounds.



(Benzyl bromide)



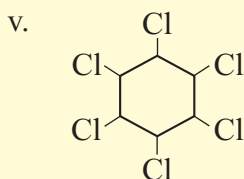
(Freon - 12)



(Hexachlorobenzene)



(Westrosol)



(Hexachlorocyclohexane)

The parent family of organic compounds is hydrocarbon. Replacement of hydrogen atom/s in aliphatic or aromatic hydrocarbons by halogen atom/s results in the formation of halogen derivatives of hydrocarbons.

In this chapter we will study halogen derivatives in a systematic way.

### Internet my friend

Find out the structures of two thyroid hormones T3 (triiodothyronine) and T4 (thyroxine). How do these help our body ?



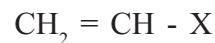
### 10.1 Classification of halogen derivatives :

Halogen derivatives of hydrocarbons are classified mainly in two ways.

**a.** On the basis of hydrocarbon skeleton to which halogen atom is bonded, the halogen derivatives are classified as **haloalkanes**, **haloalkenes**, **haloalkynes** and **haloarenes**.



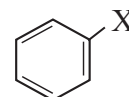
(Haloalkane)



(Haloalkene)

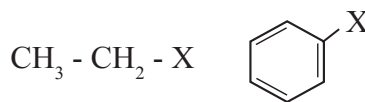


(Haloalkyne)

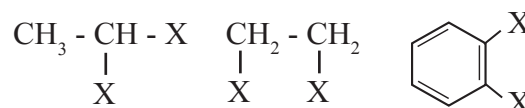


(Haloarene)

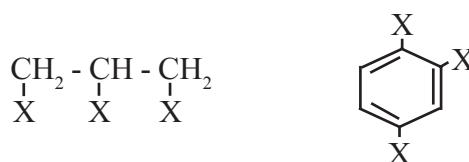
**b.** On the basis of number of halogen atoms, halogen derivatives are classified as mono, di, tri or poly halogen compounds.



Monohalogen compounds



Dihalogen compounds

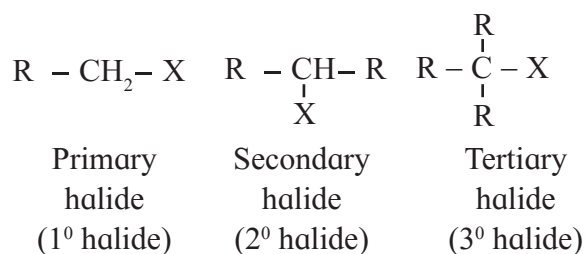


Trihalogen compounds

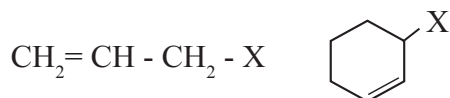
We will consider classification of mono halogen derivatives in more detail.

**10.1.1 Classification of monohalogen compounds :** Monohalogen compounds are further classified on the basis of position of halogen atom and the type of hybridization of carbon to which halogen is attached.

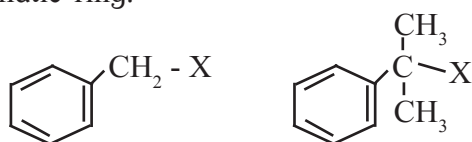
**a. Alkyl halides or haloalkanes :** In alkyl halides or haloalkanes the halogen atom is bonded to  $\text{sp}^3$  hybridized carbon which is a part of saturated carbon skeleton. Alkyl halides may be primary, secondary or tertiary depending on the substitution state of the carbon to which halogen is attached : (Refer to Std. XI Chemistry Textbook, section 14.3).



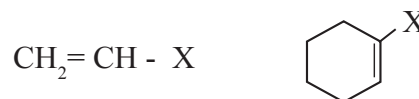
**b. Allylic halides :** In allylic halides, halogen atom is bonded to a  $\text{sp}^3$  hybridized carbon atom next to a carbon-carbon double bond.



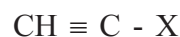
**c. Benzylic halide :** In benzylic halides halogen atom is bonded to a  $\text{sp}^3$  hybridized carbon atom which is further bonded to an aromatic ring.



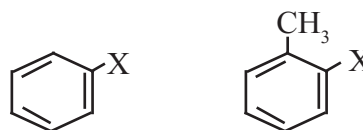
**d. Vinylic halides :** In vinylic halides halogen atom is bonded to a  $\text{sp}^2$  hybridized carbon atom of aliphatic chain. Vinylic halide is a **haloalkene**.



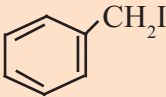
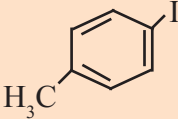
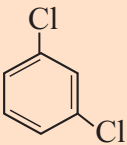
**e. Haloalkyne :** When a halogen atom is bonded to a  $\text{sp}$  hybridized carbon atom it is a haloalkyne.



**f. Aryl halides or haloarenes :** In aryl halides, halogen atom is directly bonded to the  $\text{sp}^2$  hybridized carbon atom of an aromatic ring.

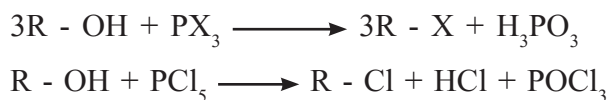


**Table 10.1 Names of some halogen derivatives**

Formula	Common name	IUPAC name
$\text{CH}_2\text{Cl}_2$	Methylene chloride	Dichloromethane
$\text{CH}_3\text{CH}_2\text{Br}$	Ethyl bromide	Bromoethane
$\text{CH}_3\text{CH}(\text{Cl})\text{CH}_3$	Isopropyl chloride	2-Chloropropane
$(\text{CH}_3)_2\text{CH} - \text{CH}_2\text{Br}$	Isobutyl bromide	1-Bromo-2-methylpropane
$(\text{CH}_3)_3\text{CBr}$	Tert-butyl bromide	2-Bromo-2-methylpropane
$(\text{CH}_3)_3\text{CCH}_2\text{Cl}$	Neopentyl chloride	1-Chloro-2, 2-dimethyl propane
$\text{CH}_2 = \text{CH} - \text{Cl}$	Vinyl chloride	1-Chloroethene
$\text{CH}_2 = \text{CH} - \text{CH}_2\text{Br}$	Allyl bromide	3-Bromopropene
$\text{CH} \equiv \text{C} - \text{Cl}$	Chloro acetylene	Chloroethyne
	Benzyl iodide	Iodophenylmethane
	p-Iodotoluene	1-Iodo-4-methyl benzene or 4-Iodotoluene
	m-dichlorobenzene	1, 3-dichlorobenzene



**b. By using phosphorous halide :** An alkyl halide may be prepared by action of phosphorous halide on alcohol. Phosphorous tribromide and triiodide are usually generated *in situ* (produced in the reaction mixture) by the action of red phosphorous on bromine and iodine respectively. Phosphorous pentachloride reacts with alcohol to give alkyl chloride.



#### Do you know ?

Some times during replacement of -OH by -X, alcohols tend to undergo rearrangement. This tendency can be minimized by use of phosphorous halides. Straight chain primary alcohols react with phosphorous trihalide to give unrearranged alkyl halides.

**c. By using thionyl chloride :** Thionyl chloride reacts with straight chain primary alcohols to give unrearranged alkyl chloride. The byproducts obtained are gases. There is **no need to put extra efforts for its separation**. Therefore this method is preferred for preparation of alkyl chloride.



#### Can you recall ?

Identify the products of the following reactions.

- $CH_4 + Cl_2 \xrightarrow{h\nu} ?$
- $CH_3-CH=CH_2 \xrightarrow{HCl} ?$
- $CH_3-CH=CH_2 + HBr \xrightarrow{\text{Peroxide}} ?$
- $CH_2=CH-CH_3 + Br_2 \xrightarrow{CCl_4} ?$

#### 10.3.2 From hydrocarbon

Alkyl halides are formed from saturated as well as unsaturated hydrocarbons by various reactions. Halogenation of alkanes is not suitable for preparation of alkyl halides as a mixture of mono and poly halogen compounds is formed.

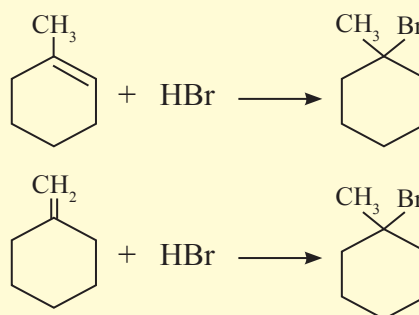
#### Addition of hydrogen halide to alkene

Alkyl halides are formed on addition of hydrogen halide to alkenes. Refer to Std XI Chemistry Textbook Chapter 15, section 15.2.4 for all the details including **order of reactivity of HX**, **Markownikov rule** and **peroxide effect**.

**Problem 10.1 :** How will you obtain 1-bromo-1-methylcyclohexane from alkene?

Write possible structures of alkene and the reaction involved.

**Solution :**



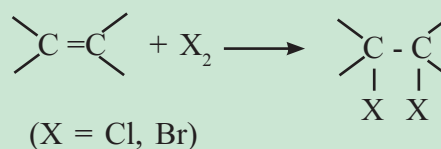
#### Use your brain power

Rewrite the following reaction by filling the blanks :

- $CH_3-CH=CH_2 + HBr \longrightarrow \dots + \dots$   
(major)(minor)
- $(CH_3)_2C=CHCH_3 + HBr \xrightarrow{\text{peroxide}} \dots + \dots$   
(major)(minor)
- $CH_3-CH=CH_2 + HBr \xrightarrow{\text{peroxide}} \dots + \dots$   
(major)(minor)

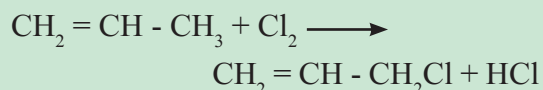
#### Do you know ?

Alkenes form addition product, vicinal dihalide, with chlorine or bromine usually in inert solvent like  $CCl_4$  at room temperature.

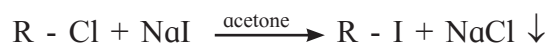


### Do you know ?

When alkenes are heated with  $\text{Br}_2$  or  $\text{Cl}_2$  at high temperature, hydrogen atom of allylic carbon is substituted with halogen atom giving allyl halide.



**10.3.3 Halogen exchange :** Alkyl iodides are prepared conveniently by treating alkyl chlorides or bromides with sodium iodide in methanol or acetone solution. The sodium bromide or sodium chloride precipitates from the solution and can be separated by filtration.



The reaction is known as **Finkelstein reaction**.

Alkyl fluorides are prepared by heating alkyl chlorides or bromides with metal fluorides such as  $\text{AgF}$ ,  $\text{Hg}_2\text{F}_2$ ,  $\text{AsF}_3$ ,  $\text{SbF}_3$  etc.

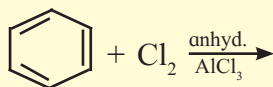


The reaction is known as **Swartz reaction**.

### 10.3.4 Electrophilic substitution :

#### Can you recall ?

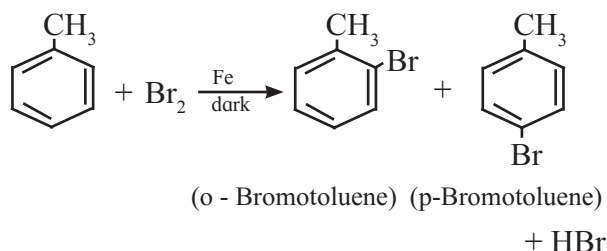
- Identify the product of the following reaction.



- Name the type of halide produced in the above reaction.
- What type of reactions are shown by benzene ?

Aryl chlorides and bromides can be prepared by direct halogenation of benzene and its derivatives through electrophilic substitution. It may be conveniently carried out in dark at ordinary temperature in presence of suitable Lewis acid catalyst like  $\text{Fe}$ ,  $\text{FeCl}_3$  or anhydrous  $\text{AlCl}_3$ .

When toluene is brominated in presence of iron, a mixture of ortho and para bromo toluene is obtained.



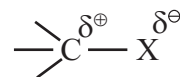
Aromatic electrophilic substitution with iodine is reversible. In this case use of  $\text{HNO}_3/\text{HIO}_4$  removes  $\text{HI}$  by oxidation to  $\text{I}_2$ , equilibrium is shifted to right and iodo product is formed.  $\text{F}_2$  being highly reactive, fluoro compounds are not prepared by this method.

**10.3.5 Sandmeyer's reaction :** Aryl halides are most commonly prepared by replacement of nitrogen of diazonium salt. (For details refer to Chapter 13 section 13.6).

**10.4 Physical properties :** Physical properties of alkyl halides are considerably different from those of corresponding alkanes. The boiling points of alkyl halides are determined by polarity of the  $\text{C-X}$  bond as well as the size of halogen atoms.

**10.4.1 Nature of intermolecular forces:** Halogens ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$  and  $\text{I}$ ) are more electronegative than carbon.

Carbon atom that carries halogen develops a partial positive charge while the halogen carries a partial negative charge. Thus carbon-halogen bond in alkyl halide is a polar covalent bond. Therefore alkyl halides are moderately polar compounds.



Size of the halogen atom increases from fluorine to iodine. Hence the  $\text{C-X}$  bond length increases. The  $\text{C-X}$  bond strength decreases with an increase in size of halogen. This is because as the size of p-orbital of halogen increases the p-orbital becomes more diffused

and the extent of overlap with orbital of carbon decreases. Some typical bond lengths, bond enthalpies and dipole moments of C-X bond are given in Table 10.2.

**Table 10.2 : Bond parameters of C-X bond**

Bond	Bond length (pm)	Bond enthalpy (kJ mol <sup>-1</sup> )	Dipole moment (debye)
CH <sub>3</sub> - F	139	452	1.847
CH <sub>3</sub> - Cl	178	351	1.860
CH <sub>3</sub> - Br	193	293	1.830
CH <sub>3</sub> - I	214	234	1.636

**10.4.2 Boiling point :** Boiling points of alkyl halides are considerably higher than those of corresponding alkanes due to higher polarity and higher molecular mass. Within alkyl halides, for a given alkyl group, the boiling point increases with increasing atomic mass of halogen, because magnitude of van der Waals force increases with increase in size and mass of halogen.

Thus boiling point of alkyl halide decreases in the order RI > RBr > RCl > RF

For example, :

Haloalkane	CH <sub>3</sub> F	CH <sub>3</sub> Cl	CH <sub>3</sub> Br	CH <sub>3</sub> I
Boiling point (K)	194.6	248.8	276.6	315.4

For the given halogen, boiling point rises with increasing carbon number.

For example,

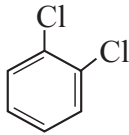
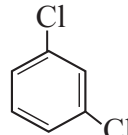
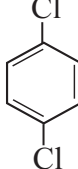
Haloalkane	Boiling point (K)
CH <sub>3</sub> Cl	248.8
CH <sub>3</sub> CH <sub>2</sub> Cl	285.5
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	320.0
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	351.5

For isomeric alkyl halides, boiling point decrease with increased branching as surface area decreases on branching and van der Waals forces decrease. For example :

Haloalkane	Boiling point (K)
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br	375
CH <sub>3</sub> - CH - CH <sub>2</sub> - CH <sub>3</sub>   Br	364
CH <sub>3</sub> - C - CH <sub>3</sub>   Br CH <sub>3</sub>	346

**10.4.3 Solubility :** Though alkyl halides are moderately polar, they are insoluble in water. It is due to inability of alkyl halides to form hydrogen bonds with water. Attraction between alkyl halide molecules is stronger than attraction between alkyl halide and water. Alkyl halides are soluble in non-polar organic solvents.

Aryl halides are also insoluble in water but soluble in organic solvents. If aryl halides are not modified by presence of any other functional group, they show properties similar to corresponding alkyl halides. The isomeric dihalobenzenes have nearly the same boiling points, but melting points of these isomers show variation. Melting point of para isomer is quite high compared to that of ortho or meta isomer. This is because of its symmetrical structure which can easily pack closely in the crystal lattice. As a result intermolecular forces of attraction are stronger and therefore greater energy is required to overcome its lattice energy.

			
b.p./K	453	446	448
m.p./K	256	249	323



**Problem 10.2** Arrange the following compounds in order of increasing boiling points : bromoform, chloromethane, dibromomethane, bromomethane.

**Solution :** The comparative boiling points of halogen derivatives are mainly related with van der Waals forces of attraction which depend upon the molecular size. In the present case all the compounds contain only one carbon. Thus the molecular size depends upon the size of halogen and number of halogen atoms present.

Thus increasing order of boiling point is,  
 $\text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_2\text{Br}_2 < \text{CHBr}_3$

## 10.5 Optical isomerism in halogen derivatives :

### Can you recall ?

- What is the relationship between two compounds having the same molecular formula?
- What is meant by stereoisomerism ?



Isomers having the same bond connectivities, that is, structural formula are called stereoisomers. Knowledge of optical isomerism, which is a kind of stereoisomerism will be useful to understand nucleophilic substitution reactions of alkyl halides (see 10.6.3).

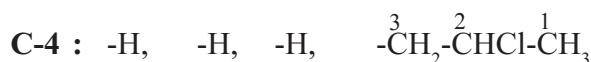
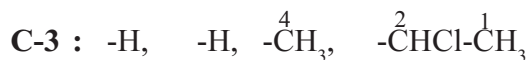
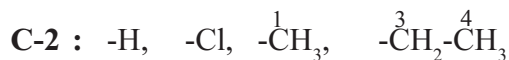
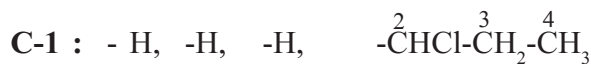
### 10.5.1 Chiral atom and molecular chirality

#### Try this...

- Make a three - dimensional model of 2 - chlorobutane.
- Make another model which is a mirror image of the first model.
- Try to superimpose the two models on each other.
- Do they superimpose on each other exactly ?
- Comment on whether the two models are identical or not.

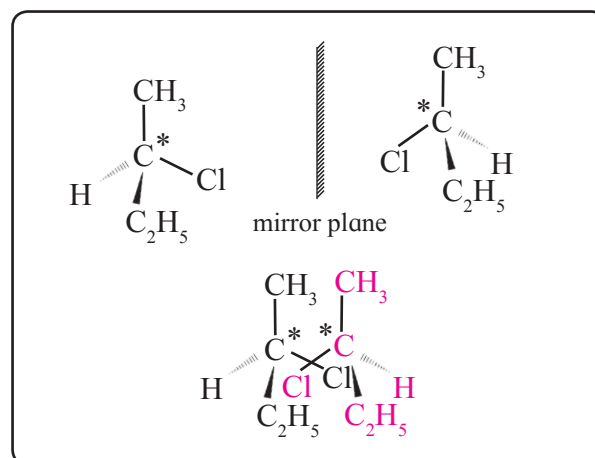


Let us, now, jot down the atoms/groups attached to each carbon in 2 - chlorobutane.



It can be seen that the four groups bonded to C-2 are all different from each other. **Carbon atom in a molecule which carries four different groups/atoms is called chiral carbon atom.** Thus, the C-2 in 2-chlorobutane is a chiral carbon. Chiral atom in a molecule is marked with asterisk (\*). For example,  $\text{CH}_3\text{-*CHCl-CH}_2\text{-CH}_3$ .

When a molecule contains one chiral atom, it acquires a unique property. Such a molecule can not superimpose perfectly on its mirror image. It is called **chiral** molecule. A chiral molecule and its mirror image are not identical (see Fig. 10.1).



**Fig. 10.1 : Nonsuperimposable mirror images**

A chiral molecule and its mirror image both have the same structural formula and, of course, the same molecular formula. The spatial arrangement of the four different groups around the chiral atom, however, is different. In other words, a chiral molecule and its mirror image are stereoisomers of each

other. (Refer to Std. XI Chemistry Textbook, Chapter 14).

The relationship between a chiral molecule and its mirror image is similar to the relationship between left and right hands. Therefore it is called **handedness** or **chirality**. (Origin : Greek word : Cheir means hand)

The stereoisomerism in which the isomers have different spatial arrangements of groups/atoms around a chiral atom is called **optical isomerism**. The optical isomers differ from each other in terms of a measurable property called **optical activity**.

To understand optical activity, we must know what is **plane polarized light**.

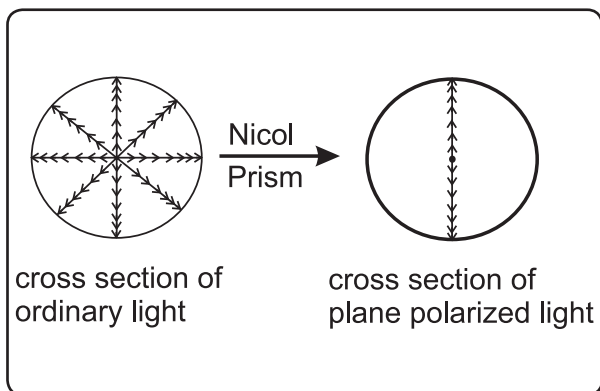
#### Remember...

The phenomenon of optical isomerism in organic compounds was observed first and its origin in molecular chirality was recognized later.



**10.5.2 Plane polarized light :** An ordinary light consists of electromagnetic waves having oscillations of electric and magnetic field in all possible planes perpendicular to direction of propagation of light.

When ordinary light is passed through Nicol's prism, oscillations only in one plane emerge out. Such a **light having oscillations only in one plane perpendicular to direction of propagation of light is known as plane polarized light**.



#### Do you know ?

Nicol prism is a special type of prism made from pieces of calcite, a crystalline form of  $\text{CaCO}_3$ , arranged in a specific manner. Nicol prism is also called polarizer.

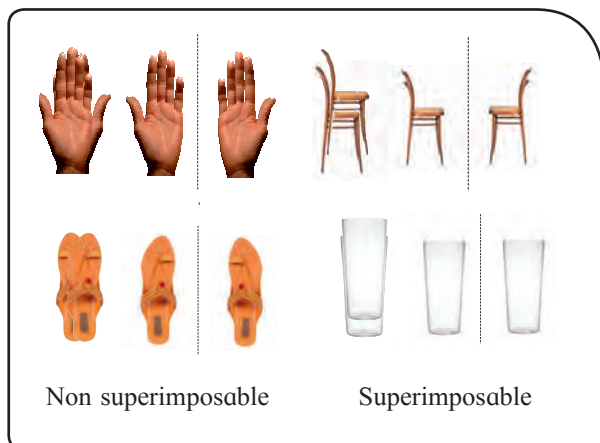


**10.5.3 Optical activity :** When an aqueous solution of certain organic compounds like sugar, lactic acid is placed in the path of plane polarized light, the transmitted light has oscillations in a different plane than the original. In other words, the incident light undergoes rotation of its plane of polarization. The plane of polarization rotates either to the right (clockwise) or to the left (anticlockwise). This property of a substance by which it **rotates plane of polarization of incident plane polarized light is known as optical activity**. The compounds which rotate the plane of plane polarized light are called **optically active compounds** and those which do not rotate it are optically inactive compounds. Optical activity of a substance is expressed numerically in terms of **optical rotation**. The angle through which a substance rotates the plane of plane polarized light on passing through it is called optical rotation. In accordance with the direction of optical rotation an optically active substance is either dextrorotatory or laevorotatory. A compound which rotates the plane of plane polarized light towards right is called **dextrorotatory** and designated by symbol **d-** or by **(+)** sign. A compound which rotates plane of plane polarized light towards left is called **laevorotatory** and designated by symbol **l-** or by **(-)** sign.

Isomerism in which isomeric compounds have different optical activity is known as **optical isomerism**. French scientist Louis Pasteur first recognized that optical activity is associated with certain type of 3-dimensional structure of molecules. Pasteur introduced the term **enantiomers** for the optical isomers having equal and opposite optical rotation.



Figure 10.2 indicates a few objects in our day to day life which exhibit superimposable and non-superimposable mirror image relationship.



**Fig. 10.2 : Superimposable and nonsuperimposable mirror image**

#### Remember...

- Optical activity is an experimentally observable property of compounds. Chirality is a description of molecular structure. Optical activity is the consequence of chirality.
- Molecules which contain one chiral atom are chiral, that is, they are nonsuperimposable on their mirror image.
- The two non-superimposable mirror image structures are called **pair of enantiomers**.
- Enantiomers have **equal and opposite optical rotation**. Thus, enantiomers are a kind of optical isomers.

**10.5.4 Enantiomers :** The optical isomers which are non-superimposable mirror image of each other are called **enantiomers** or **enantiomorphs** or **optical antipodes**. For example, 2 - chlorobutane exists as a pair of enantiomers (Fig. 10.1).

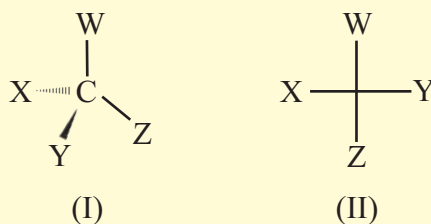
Enantiomers have identical physical properties (Such as melting point, boiling points, densities, refractive index) except the sign of optical rotation. The magnitude of their optical rotation is equal but the sign of optical rotation is opposite. They have identical chemical properties except towards optically active reagent.

An equimolar mixture of enantiomers (dextrorotatory and laevorotatory) is called **racemic modification or racemic mixture**. A racemic modification is optically inactive because optical rotation due to molecules of one enantiomer is cancelled by equal and opposite optical rotation due to molecules of the other enantiomer. A racemic modification is designated as (*dl*) or by ( $\pm$ ) sign.

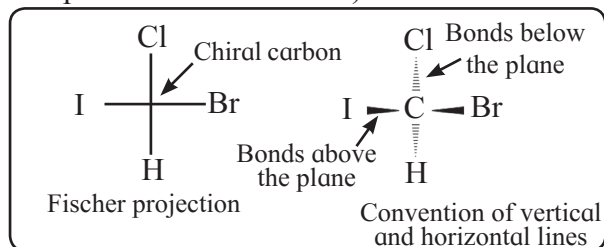
#### 10.5.5 Representation of configuration of molecules :

##### Can you recall ?

- Identify the type of following 3-D representation (I) and (II) of a molecule and state significance of the lines drawn.

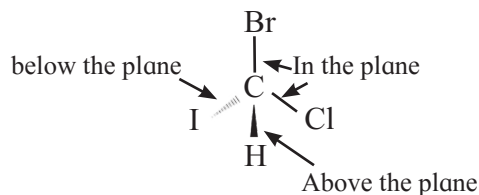


**a. Fischer projection formula (cross formula) :** Two representations are used to represent configuration of chiral carbon and the 3-dimensional structure of optical isomers on plane paper. These are (a) wedge formula and (b) Fischer projection formula (also called cross formula) (Std. XI Chemistry Textbook Chapter 14 section 14.2.3).



**Fig. 10.3 Fischer projection formula**

**b. Wedge formula :** When a tetrahedral carbon is imagined to be present in the plane of paper all the four bonds at this carbon cannot lie in the same plane. The bonds in the plane of paper are represented by normal lines, the bonds projecting above the plane of paper are represented by solid wedges (or simply by bold lines) while bonds going below the plane of paper are represented by broken wedges (or simply by broken lines).



### Try this...

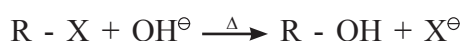
1. Draw structures of enantiomers of lactic acid ( $\text{CH}_3\text{-CH}(\text{OH})\text{-COOH}$ ) using Fischer projection formulae.
2. Draw structures of enantiomers of 2-bromobutane using wedge formula.



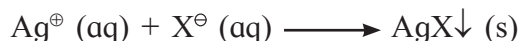
## 10.6 Chemical properties :

### 10.6.1 Laboratory test of haloalkanes :

Haloalkanes are of neutral type in aqueous medium. On warming with aqueous sodium or potassium hydroxide the covalently bonded halogen in haloalkane is converted to halide ion.



When this reaction mixture is acidified by adding dilute nitric acid and silver nitrate solution is added a precipitate of silver halide is formed which confirms presence of halogen in the original organic compound.



### 10.6.2 Nucleophilic substitution reactions of haloalkanes :

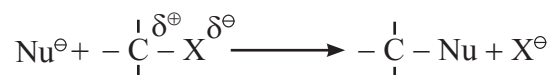
When a group bonded to a carbon in a substrate is replaced by another group to get a product with no change in state of

### Can you recall ?



- What is meant by substitution reaction ?
- Can you identify substitution reaction from the following ?  
 (i)  $\text{CH}_3 - \text{CH}_2 - \text{OH} + \text{HCl} \xrightarrow{\text{ZnCl}_2} \text{CH}_3 - \text{CH}_2 - \text{Cl} + \text{H}_2\text{O}$   
 (ii)  $\text{CH}_2 = \text{CH}_2 + \text{HI} \longrightarrow \text{CH}_3 - \text{CH}_2 - \text{I}$
- Is the carbon carrying halogen in alkyl halide, an electrophilic or a nucleophilic centre ?

hybridization of that carbon the reaction is called **substitution reaction**. The C-X bond in alkyl halides is a polar covalent bond and the carbon in C-X bond is positively polarized. In other words, the **C-X carbon** is an **electrophilic centre**. It has, therefore, a tendency to react with a nucleophile. (Refer to Std. XI Chemistry Textbook Chapter 14.) Alkyl halides react with a variety of nucleophiles to give **nucleophilic substitution reactions** ( $\text{S}_\text{N}$ ). The reaction is represented in general form as shown below.



When a substrate reacts fast it is said to be reactive. The reactivity of alkyl halides in  $\text{S}_\text{N}$  reaction depends upon two factors, namely, the substitution state ( $1^\circ$ ,  $2^\circ$  or  $3^\circ$ ) of the carbon and the nature of the halogen. The order of reactivity influenced by these two factors is as shown below.

tertiary alkyl halide ( $3^\circ$ ) > secondary alkyl halide ( $2^\circ$ ) > primary alkyl halide ( $1^\circ$ ) and  $\text{R} - \text{I} > \text{R} - \text{Br} > \text{R} - \text{Cl}$

Examples of some important nucleophilic substitution reactions of alkyl halides are shown in Table 10.3.

### 10.3 Nucleophilic substitution reactions of alkyl halides

Sr. No.	Alkyl halide	Reagent	Substitution product
1.	R - X +	$\text{NaOH(aq)} \xrightarrow{\Delta}$ (or KOH)	R - OH + NaX (alcohol) (or KX)
2.	R - X +	$\text{NaOR}' \xrightarrow{\Delta}$ (sodium alkoxide)	R - O - R' + NaX (ether)
3.	R - X +	$\text{R}' - \overset{\text{O}}{\parallel} \text{C} - \overset{\ominus}{\text{O}}\overset{\oplus}{\text{Ag}} \xrightarrow{\Delta}$ (silver carboxylate)	$\text{R}' - \overset{\text{O}}{\parallel} \text{C} - \text{OR} + \text{AgX} \downarrow$ (ester)
4.	R - X +	$\text{NH}_3(\text{alc.}) \xrightarrow[\text{(excess)}]{\text{pressure}}$	R - NH <sub>2</sub> + HX (primary amine)
5.	R - X +	$\text{KCN (alc.)} \xrightarrow{\Delta}$	R - CN + KX (nitrile)(alkyl cyanide)
6.	R - X +	$\text{AgCN (alc.)} \xrightarrow{\Delta}$	R - N $\equiv$ C + AgX $\downarrow$ (isocyanide)
7.	R - X +	$\text{K}\overset{\oplus}{\text{O}} - \text{N} = \text{O} \longrightarrow$ (potassium nitrite)	R - O - N = O + KX (alkyl nitrite)
8.	R - X +	$\text{Ag} - \text{O} - \text{N} = \text{O} \longrightarrow$ (silver nitrite)	$\text{R} - \overset{\oplus}{\text{N}} \begin{matrix} \text{O} \\ \text{O} \end{matrix} + \text{AgX} \downarrow$ (nitroalkane)

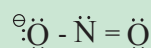
#### Do you know ?

Cyanide ion is capable of attacking through more than one site (atom).



Such nucleophiles are called ambident nucleophiles. KCN is predominantly ionic ( $\text{K}^+\text{C}^{\ominus} \equiv \ddot{\text{N}}^-$ ) and provides cyanide ions. Both carbon and nitrogen are capable of donating electron pair. C-C Bond being stronger than C-N bond, attack occurs through carbon atom of cyanide group forming alkyl cyanides as major product. However AgCN ( $\text{Ag}-\text{C} \equiv \ddot{\text{N}}^-$ ) is mainly covalent compound and nitrogen is free to donate pair of electron. Hence attack occurs through nitrogen resulting in formation of isocyanide.

Another ambident nucleophile is nitrite ion, which can attack through 'O' or 'N'.



#### Can you tell ?

Alkyl halides when treated with alcoholic solution of silver nitrite give nitroalkanes whereas with sodium nitrite they give alkyl nitrites Explain.

#### 10.6.3 Mechanism of S<sub>N</sub> reaction :

#### Can you recall ?

- What is meant by order and molecularity of a reaction ?
- What is meant by mechanism of chemical reaction ?

It can be seen from the Table 10.3 that in nucleophilic substitution reactions of alkyl halides the halogen atom gets detached from the carbon and a new bond is formed between that electrophilic carbon and nucleophile. The covalently bonded halogen is converted into halide ion ( $\text{X}^-$ ). It means that the two electrons constituting the original covalent bond are carried away by the halogen along with it. The halogen atom of alkyl halide is, therefore, called '**leaving group**' in the

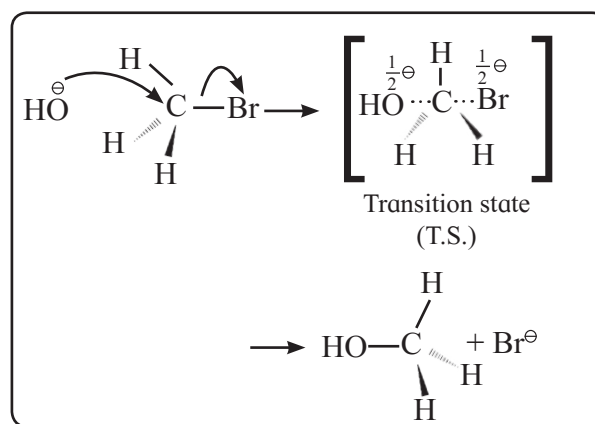
context of this reaction. Leaving group is the group which leaves the carbon by taking away the bond pair of electrons. The substrate undergoes two changes during a  $S_N$  reaction. The original C-X bond undergoes heterolysis and a new bond is formed between the carbon and the nucleophile using two electrons of the nucleophile. These changes may occur in one or more steps. The description regarding the sequence and the way in which these two changes take place in  $S_N$  reaction is called mechanism of  $S_N$  reaction. The mechanism is deduced from the results of study of kinetics of  $S_N$  reactions. Two mechanisms are observed in various  $S_N$  reactions. These are denoted as  $S_N1$  and  $S_N2$  mechanisms.

**a.  $S_N2$  Mechanism :** The reaction between methyl bromide and hydroxide ion to give methanol follows a second order kinetics, that is, the rate of this reaction depends on concentration of two reacting species, namely, methyl bromide and hydroxide. Hence it is called **substitution nucleophilic bimolecular,  $S_N2$** .



$$\text{rate} = k [\text{CH}_3\text{Br}] [\text{OH}^\ominus]$$

Rate of a chemical reaction is influenced by the chemical species taking part in the slowest step of its mechanism. In the above reaction only two reactants are present and both are found to influence the rate of the reaction. This means that the reaction is a single step reaction which can also be called the slow step. This further implies that the two changes, namely, bond breaking and bond forming at the carbon take place simultaneously. This  $S_N2$  mechanism is represented as shown in Fig. 10.4.

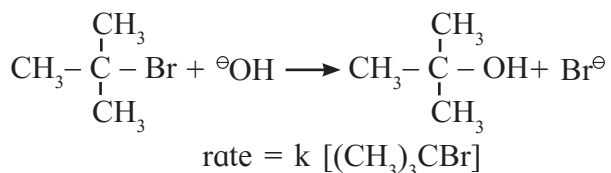


**Fig. 10.4 :  $S_N2$  mechanism**

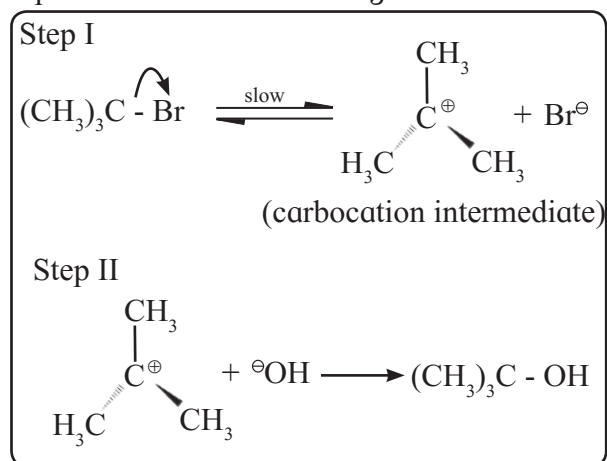
**Salient features of  $S_N2$  mechanism :**

- Single step mechanism** with simultaneous bond breaking and bond forming.
- Backside attack of nucleophile :** The nucleophile attacks the carbon undergoing substitution from the side opposite to that of the leaving group. This is to avoid steric repulsion (repulsion due to bulkiness of the groups) and electrostatic repulsion between the incoming nucleophile and the leaving group.
- In the transition state (T.S.) the nucleophile and leaving groups are bonded to the carbon with partial bonds and carry partial negative charge. (Thus, the total negative charge is diffused.)
- The T.S. contains **pentacoordinate carbon** having three  $\sigma$  (sigma) bonds in one plane making bond angles of  $120^\circ$  with each other and two partial covalent bonds along a line perpendicular to this plane.
- When  $S_N2$  reaction is brought about at chiral carbon (in an optically active substrate), the product is found to have opposite configuration compared to that of the substrate. In other words,  $S_N2$  reaction is found to proceed with inversion of configuration. This is like flipping of an umbrella (See Fig. 10.4). It is known as **Walden inversion**. The inversion in configuration is the result of backside attack of the nucleophile.

**b. S<sub>N</sub>1 Mechanism :** The reaction between tert-butyl bromide and hydroxide ion to give tert-butyl alcohol follows a first-order kinetics, that is the rate of this reaction depends on concentration of only one species, which is the substrate molecule, tert-butyl bromide. Hence it is called **substitution nucleophilic unimolecular, S<sub>N</sub>1**.



It can be seen in this reaction that concentration of only substrate appears in the rate equation; concentration of the nucleophile does not influence the reaction rate. In other words, tert-butyl bromide reacts with hydroxide by a two step mechanism. In the slow step C-X bond in the substrate undergoes heterolysis and in the subsequent fast step the nucleophile uses its electron pair to form a new bond with the carbon undergoing change. This S<sub>N</sub>1 mechanism is represented as shown in Fig. 10.5.



**Fig. 10.5 : S<sub>N</sub>1 mechanism**

**Salient features of S<sub>N</sub>1 mechanism :**

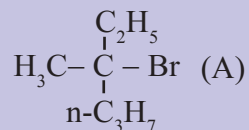
- Two step** mechanism.
- Heterolysis** of C-X bond in the slow and reversible first step to form **planar carbocation intermediate**.
- Attack of the nucleophile** on the carbocation intermediate in the fast second step to form the product.

- When S<sub>N</sub>1 reaction is carried out at chiral carbon in an optically active substrate, the product formed is nearly racemic. This indicates that S<sub>N</sub>1 reaction proceeds **mainly** with **racemization**. This means both the enantiomers of product are formed in almost equal amount. Racemization in S<sub>N</sub>1 reaction is the result of formation of planar carbocation intermediate (Fig. 10.5). Nucleophile can attack planar carbocation from either side which results in formation of both the enantiomers of the product.

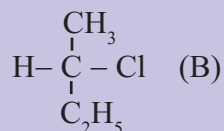
#### Use your brain power



- Draw the Fischer projection formulae of two products obtained when compound (A) reacts with OH<sup>⊖</sup> by S<sub>N</sub>1 mechanism.



- Draw the Fischer projection formula of the product formed when compound (B) reacts with OH<sup>⊖</sup> by S<sub>N</sub>2 mechanism.

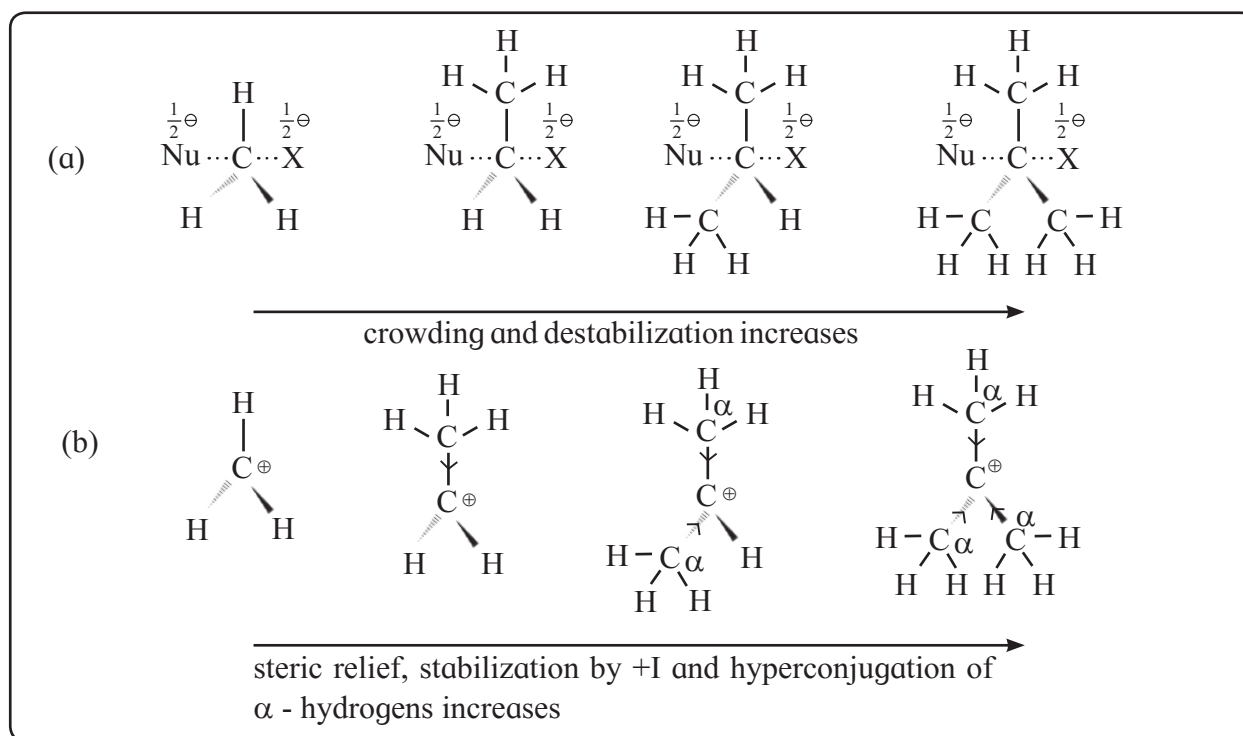


#### 10.6.4 Factors influencing S<sub>N</sub>1 and S<sub>N</sub>2 mechanism :

**a. Nature of substrate :** S<sub>N</sub>2 : The T.S. of S<sub>N</sub>2 mechanism is pentacoordinate and thus crowded (See Fig. 10.4). As a result S<sub>N</sub>2 mechanism is favoured in primary halides and least favoured in tertiary halides.

S<sub>N</sub>1 : A planar carbocation intermediate is formed in S<sub>N</sub>1 reaction. It has no steric crowding. Bulky alkyl groups can be easily accommodated in planar carbocation See (Fig. 10.5). As a result S<sub>N</sub>1 mechanism is most favoured in tertiary halides and least favoured in primary halides. (Formation of planar carbocation intermediate results in a

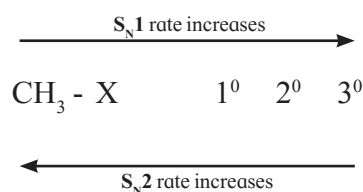




**Fig. 10.6 : Influence of substrate in  $S_N1$  and  $S_N2$  (a) Transition states (T.S.) in  $S_N2$  (b) Carbocation intermediates in  $S_N1$**

relief from steric crowding present in the tertiary halide substrate).

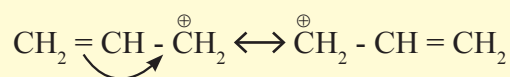
Secondly the carbocation intermediate is stabilized by +I effect of alkyl substituents and also by hyperconjugation effect of alkyl substituents containing  $\alpha$ -hydrogens. As a result,  $S_N1$  mechanism is most favoured in tertiary halides and least favoured in primary halides. This can be represented diagrammatically as shown below.



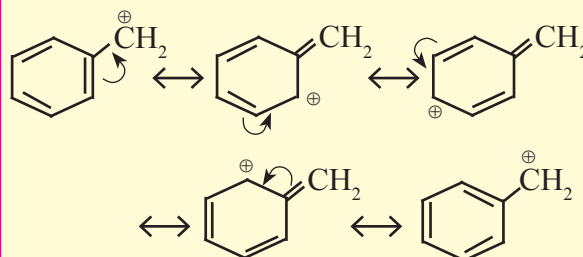
Tertiary halides undergo nucleophilic substitution by  $S_N1$  mechanism while primary halides follow  $S_N2$  mechanism. Secondary halides react by either of the mechanism or by mixed mechanism depending upon the exact conditions.

**Problem 10.4 :** Primary allylic and primary benzylic halides show higher reactivity by  $S_N1$  mechanism than other primary alkyl halides. Explain.

**Solution :**  $S_N1$  reaction involves formation of carbocation intermediate. The allylic and benzylic carbocation intermediate formed are resonance stabilized, and hence  $S_N1$  mechanism is favoured.



Resonance stabilization of allylic carbocation



Resonance stabilization of benzylic carbocation

### b. Nucleophilicity of the reagent :

#### Can you recall ?



- Give some examples of nucleophiles that are electrically neutral.
- Give some examples of anionic nucleophiles.
- What is the difference between a base and a nucleophile ?

A nucleophile is a species that uses its electron pair to form a bond with carbon. Nucleophilic character of any species is expressed in its electron releasing tendency, which can be correlated to its strength as Lewis base.

A more powerful nucleophile attacks the substrate faster and favours  $S_N2$  mechanism. The rate of  $S_N1$  mechanism is independent of the nature of nucleophile. Nucleophile does not react in slow step of  $S_N1$ . It waits till the carbocation intermediate is formed, and reacts fast with it.

#### Do you know ?



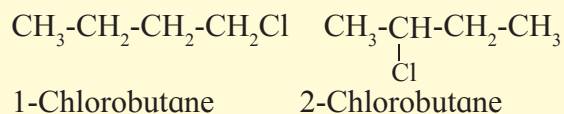
1. A negatively charged nucleophile is more powerful than its conjugate acid. For example  $R-O^-$  is better nucleophile than  $R-OH$ .
2. When donor atoms are from same period of periodic table, nucleophilicity decreases from left to right in a period. For example  $H_2\ddot{O}$  is less powerful nucleophile than  $NH_3$ .
3. When donor atoms are from same group of the periodic table, nucleophilicity increases down the group. For example,  $I^-$  is better nucleophile than  $Cl^-$ .

**c. Solvent polarity :**  $S_N1$  mechanism proceeds via formation of carbocation intermediate. A good ionizing solvent, polar solvent, stabilizes the ions by solvation. Solvation of

carbocation is relatively poor and solvation of anion is particularly important. Anions are solvated by hydrogen bonding solvents, that is, protic solvents. Thus  $S_N1$  reaction proceeds more rapidly in polar protic solvents than in aprotic solvents.

Polar protic solvents usually decrease the rate of  $S_N2$  reaction. In the rate determining step of  $S_N2$  mechanism substrate as well as nucleophile is involved. A polar solvent stabilizes nucleophile (one of the reactant) by solvation. Thus solvent deactivates the nucleophile by stabilizing it. Hence aprotic solvents or solvents of low polarity will favour  $S_N2$  mechanism.

**Problem 10.5 :** Which of the following two compounds would react faster by  $S_N2$  mechanism and Why ?



**Solution :** In  $S_N2$  mechanism, a pentacoordinate T.S. is involved. The order of reactivity of alkyl halides towards  $S_N2$  mechanism is, Primary > Secondary > Tertiary, (due to increasing crowding in T.S. from primary to tertiary halides. 1-Chlorobutane being primary halide will react faster by  $S_N2$  mechanism, than the secondary halide 2-chlorobutane.

#### Can you recall ?



- How are alkenes prepared from alkyl halides ?
- Which is stronger base from the following ?  
i. aq. KOH      ii. alc. KOH

### 10.6.5 Elimination reaction : Dehydrohalogenation

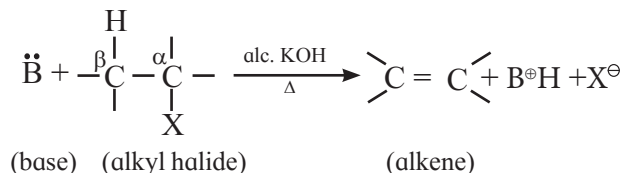
When alkyl halide having at least one  $\beta$ -hydrogen is boiled with alcoholic solution of potassium hydroxide, it undergoes elimination of hydrogen atom from  $\beta$ -carbon and halogen atom from  $\alpha$ -carbon resulting in the formation of an alkene.

#### Remember...

The carbon bearing halogen is commonly called  $\alpha$ -carbon (alpha carbon) and any carbon attached to  $\alpha$ -carbon is  $\beta$ -carbon (beta carbon). Hydrogens attached to  $\beta$ -carbon are  $\beta$ -hydrogens.

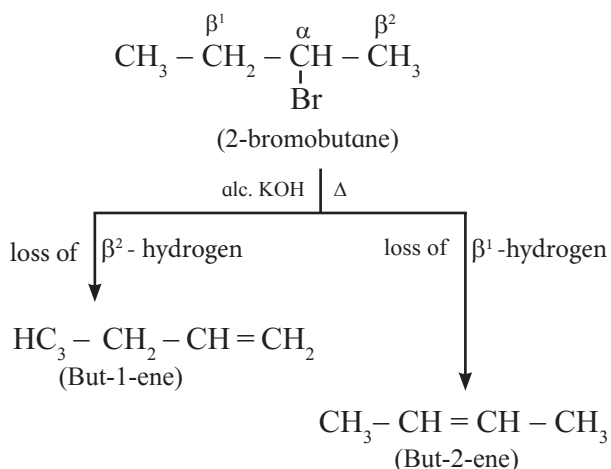


This reaction is called  $\beta$ -elimination (or 1,2 - elimination) reaction as it involves elimination of halogen and a  $\beta$  - hydrogen atom.



As hydrogen and halogen is removed in this reaction it is also known as **dehydrohalogenation** reaction.

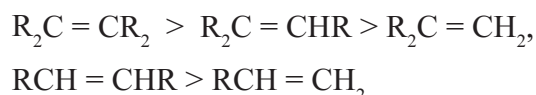
If there are two or more non-equivalent  $\beta$ -hydrogen atoms in a halide, then this reaction gives a mixture of products. Thus, 2-bromobutane on heating with alcoholic KOH gives mixture of but-1-ene and but-2-ene.



The different products of elimination do not form in equal proportion. After studying a number of elimination reactions, Russian chemist Saytzeff formulated an empirical rule given below.

**In dehydrohalogenation reaction, the preferred product is that alkene which has greater number of alkyl groups attached to doubly bonded carbon atoms.**

Therefore, in the above reaction but-2-ene is the preferred product, and is formed as the major product. It turned out that more highly substituted alkenes are also more stable alkenes. Hence **Saytzeff elimination is preferred formation of more highly stabilized alkene during an elimination reaction.** The stability order of alkyl substituted alkenes is :



#### Do you know ?

##### Elimination versus substitution:

Alkyl halides undergo substitution as well as elimination reaction. Both reactions are brought about by basic reagent, hence there is always a competition between these two reactions. The reaction which actually predominates depends upon following factors.

**a. Nature of alkyl halides :** Tertiary alkyl halides prefer to undergo elimination reaction where as primary alkyl halides prefer to undergo substitution reaction.

**b. Strength and size of nucleophile :** Bulkier electron rich species prefers to act as base by abstracting proton, thus favours elimination. Substitution is favoured in the case of comparatively weaker bases, which prefer to act as nucleophile

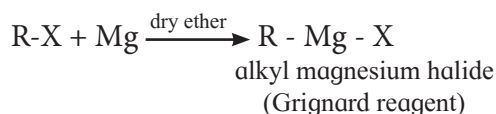
**c. Reaction conditions :** Less polar solvent, high temperature favours elimination where as low temperature, polar solvent favours substitution reaction.



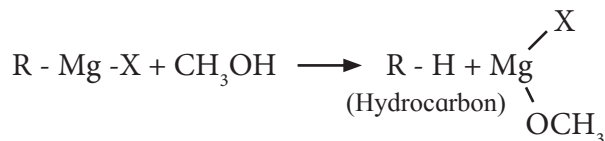
## 10.6 Reaction with active metals

Active metals like sodium, magnesium, cadmium readily combine with alkyl chlorides, bromides and iodides to form compounds containing carbon-metal bonds. These are known as organometallic compounds.

**a. Reaction with magnesium :** When alkyl halide is treated with magnesium in dry ether as solvent, it gives alkyl magnesium halide. It is known as Grignard reagent.

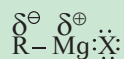


Grignard reagents are very reactive compounds. They react with water or compounds containing hydrogen attached to electronegative element.



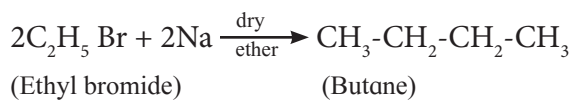
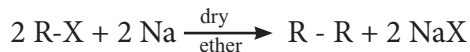
### Do you know ?

Carbon-magnesium bond in Grignard reagent is a polar covalent bond. The carbon pulls electrons from the electropositive magnesium. Hence carbon in Grignard reagent has negative polarity and acts as a nucleophile



Victor Grignard received Nobel Prize in 1912 for synthesis and study of organo-magnesium compounds. Grignard reagent is a very versatile reagent used by organic chemist. Vinyl and aryl halides also form Grignard reagent.

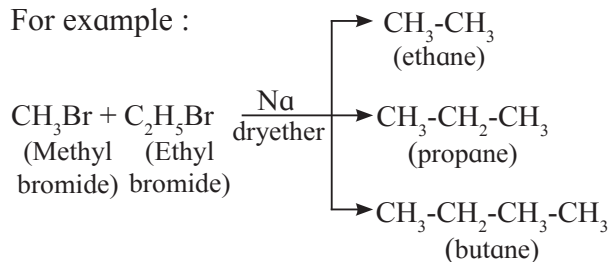
**b. Wurtz reaction :** Alkyl halides react with metallic sodium in dry ether as solvent, and form higher alkanes containing double the number of carbon atoms present in alkyl halide. This reaction is called Wurtz reaction. (Refer to Std. XI Chemistry Textbook sec. 1.5.3)



+ 2 NaBr

When a mixture of two different alkyl halides is used, all the three possible alkanes are formed.

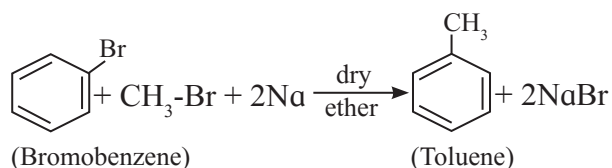
For example :



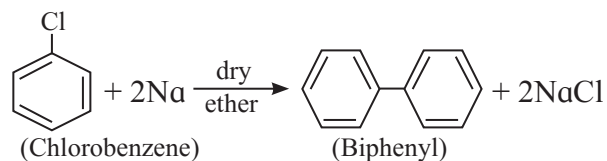
### 10.6.1 Reaction of haloarenes :

#### a. Reactions of haloarene with metals

The reaction of aryl halide with alkyl halide and sodium metal in dry ether to give substituted aromatic compounds is known as **Wurtz-Fittig reaction**. This reaction is an extension of Wurtz reaction and was carried out by Fittig. This reaction allows alkylation of aryl halides.



In case only aryl halide takes part in the reaction, the product is biphenyl and the reaction is known as **Fittig reaction**.



## b. Nucleophilic substitution $S_N$ of haloarenes:

### Can you recall ?

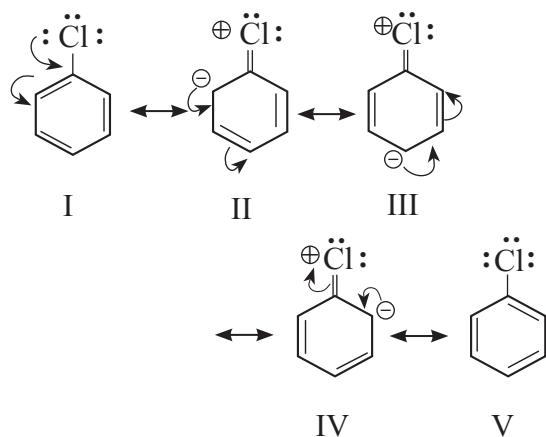
- What is resonance?
- Draw resonance structures of bromobenzene.
- Identify the type of hybridization of carbon to which halogen is attached in haloarene.



Aryl halides show low reactivity towards nucleophilic substitution reactions. The low reactivity of aryl halides is due to :

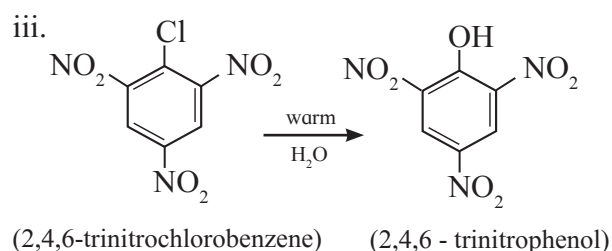
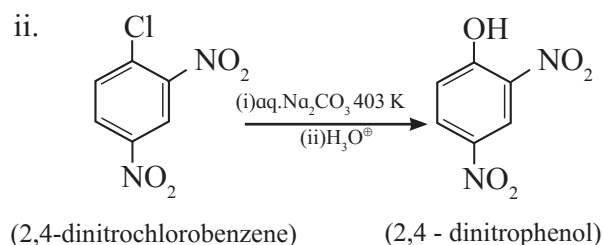
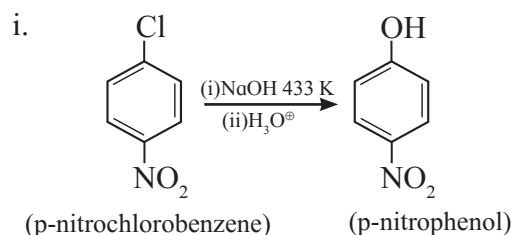
- Resonance effect and
- $sp^2$  hybrid state of C .

i. One of the lone pairs of electrons on halogen atom is in conjugation with  $\pi$  -electrons of the ring. For example the following different resonance structures can be written for chlorobenzene.



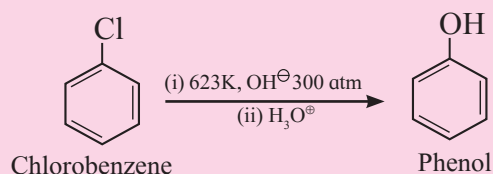
Resonance structures II, III and IV show double bond character to carbon-chlorine bond. Thus carbon-chlorine bond in chlorobenzene is stronger and shorter than chloroalkane molecule, C-Cl bond length in chlorobenzene is 169 pm as compared to C-Cl bond length in alkyl chloride 178 pm. Hence it is difficult to break. Phenyl cation produced due to self-ionization of haloarene will not be stabilised by resonance, which rules out possibility of  $S_N1$  mechanism. Back side attack of nucleophile is blocked by the aromatic ring, which rules out  $S_N2$  mechanism.

Thus nucleophilic substitution reaction involving cleavage of C-X bond in haloarene proceeds with difficulty. However, the presence of certain groups at certain positions of the ring, markedly activate the halogen of aryl halides towards substitution. For example, presence of electron withdrawing group at ortho and/or para position greatly increases the reactivity of haloarenes towards substitution of halogen atom. Greater the number of electron withdrawing groups at o/p position, greater is the reactivity. Electron withdrawing group at meta position has practically no effect on reactivity.



### Can you tell ?

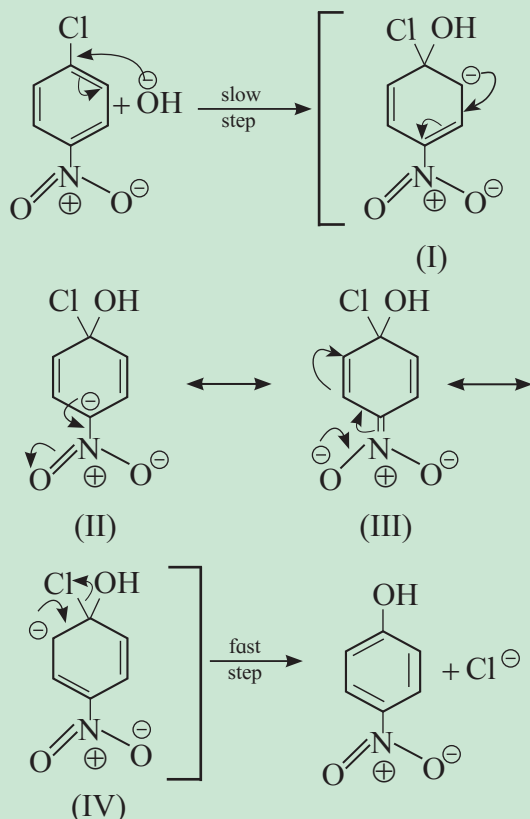
Conversion of chlorobenzene to phenol by aqueous sodium hydroxide requires high temperature of about 623K and high pressure. Explain.





### Do you know ?

Occurrence of nucleophilic substitution in p-nitrochlorobenzene can be explained on the basis of resonance stabilization of the intermediate.



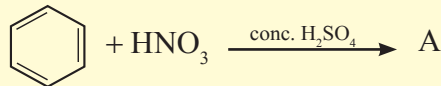
The resonance structure (III) shows that the electron withdrawing nitro group ( $-\text{NO}_2$ ) in the p-position extends the conjugation. As a result, the intermediate carbanion is better stabilized which favours nucleophilic substitution reaction.

### c. Electrophilic substitution (SE) in arylhalides

#### Can you recall ?

- What is an electrophile?
- Give some examples of electrophiles
- What type of reactions are observed in benzene?

- Identify the product A of following reaction.



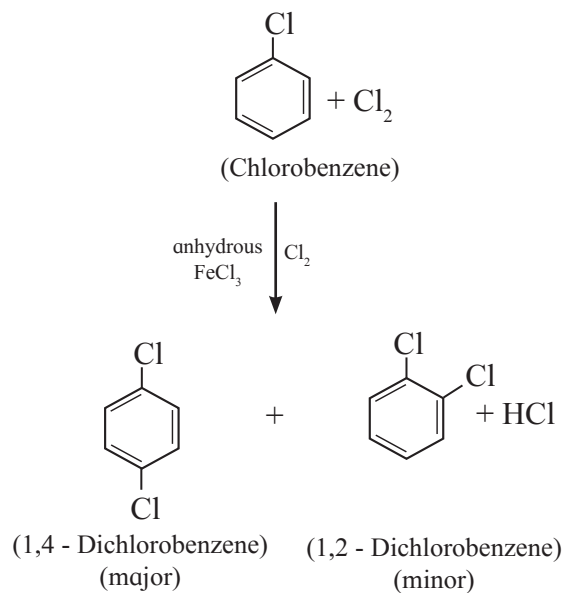
Aryl halides undergo electrophilic substitution reaction slowly as compared to benzene.

In resonance structures of chlorobenzene (see section 10.6.5) electron density is relatively more at ortho and para position. Therefore incoming electrophilic group is more likely to attack at these positions. But due to steric hinderance at ortho position, para product usually predominates. In haloarenes, halogen atom has strong electron withdrawing inductive effect (-I). This deactivates the ring and electrophilic substitution reaction occurs slowly.

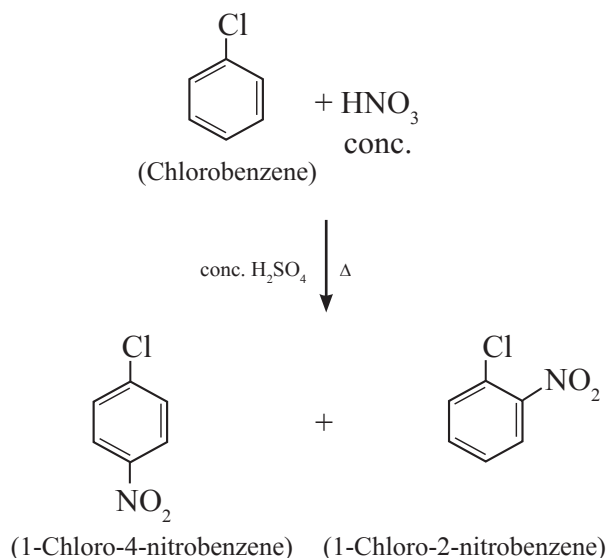
#### Remember...

The -I effect of Cl is more powerful than its +R effect. Therefore Cl is o-/p- directing but ring deactivating group.

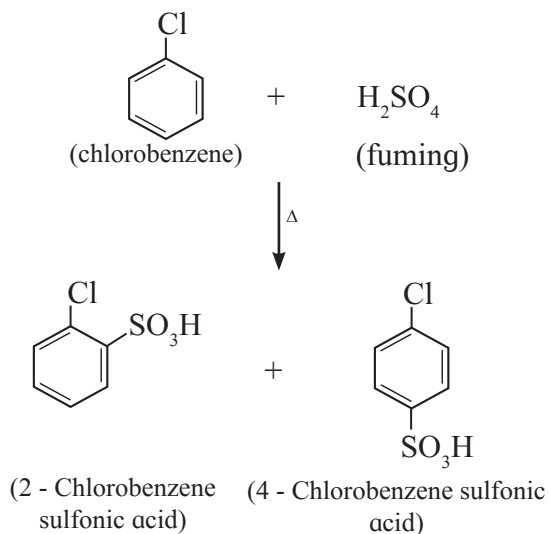
**i. Halogenation :** It is carried out by reacting haloarene with halogen in presence of ferric salt as Lewis acid catalyst.



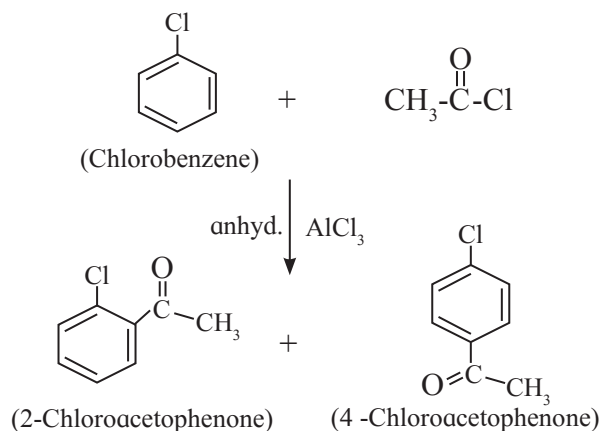
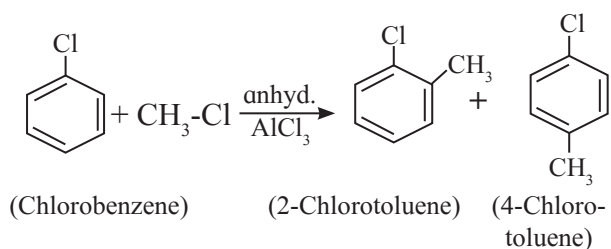
**ii. Nitration :** It is carried out by heating haloarene with conc.  $\text{HNO}_3$  in presence of conc.  $\text{H}_2\text{SO}_4$ .



**iii. Sulfonation :** It is carried out by heating haloarene with fuming  $\text{H}_2\text{SO}_4$ .



**iv. Friedel Craft's reaction :** It is carried out by treating haloarene with alkyl chloride or acyl chloride in presence of anhydrous  $\text{AlCl}_3$  as a catalyst.



## 10.7 Uses and Environmental effects of some polyhalogen compounds

**10.7.1 Dichloromethane/ methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) :** It is a colourless volatile liquid with moderately sweet aroma. It is used as a solvent, and used as a propellant in aerosols.

Over exposure to dichloromethane causes dizziness, fatigue, nausea, headaches, numbness, weakness. It is highly dangerous if it comes in direct contact with eyes as it damages cornea.

**10.7.2 Chloroform / trichloromethane ( $\text{CHCl}_3$ ) :** It is a colourless liquid with peculiar sweet smell. It is used to prepare chlorofluoromethane, a refrigerant R-22. It is used as a solvent for extraction of natural products like gums, fats, resins. It is used as a source of dichlorocarbene. Chloroform causes depression of central nervous system. Inhaling chloroform for a short time causes fatigue, dizziness and headache. Long exposure to chloroform may affect liver. Chloroform when exposed to air and light forms a poisonous compound phosgene so it is stored in dark coloured air tight bottles.

**10.7.3 Carbon tetrachloride / tetrachloromethane ( $\text{CCl}_4$ ) :**

It is a colourless liquid with sweet smell. It is very useful solvent for oils, fats, resins. It serves as a source of chlorine. It is used as a cleaning agent. It is highly toxic to liver. Exposure to high concentration of  $\text{CCl}_4$  can affect central

nervous system and it is suspected to be carcinogenic. Prolonged exposure may cause death. It is a green house gas.

#### 10.7.4 Iodoform or triiodomethane (CHI<sub>3</sub>):

It is a yellow crystalline substance with disagreeable smell. It is used in medicine as a healing agent and antiseptic in dressing of wounds, however its use is limited.

It causes irritation to skin and eyes. It may cause respiratory irritation or breathing difficulty, dizziness, nausea, depression of central nervous system, visual disturbance.

**10.7.5 Freons :** These are organic compounds of chlorine and fluorine, chlorofluorocarbons, CFC's are commonly used as refrigerants. The most common representative is dichlorodifluoromethane (Freon-12) others include chlorodifluoromethane (R-22), trichlorofluoromethane (R-11) and so on.

They are used as refrigerants in fridge and airconditioning, propellants in aerosol and solvents. They are used as blowing agents in making foams and packing materials.

Chlorofluorocarbons are responsible for ozone depletion in stratosphere. Regular large inhalation of freons results in breathing problems, organ damage, loss of consciousness.

#### Do you know ?

How do CFC destroy the ozone layer in the atmosphere ?

When ultraviolet radiation (UV) strikes CFC (CFCl<sub>3</sub>) molecules in the upper atmosphere, the carbon-chlorine bond breaks and produces highly reactive chlorine atom (Cl).



This reactive chlorine atom decomposes ozone (O<sub>3</sub>) molecule into oxygen molecule (O<sub>2</sub>).

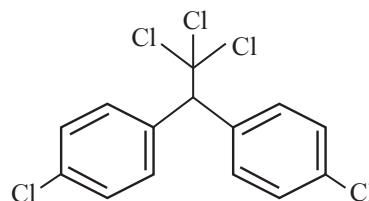


One atom of chlorine can destroy upto 100,000 ozone molecules.

**10.7.6 Dichlorodiphenyltrichloroethane (DDT) :** It is colourless, tasteless and odorless crystalline compound having insecticidal property.

It kills insects such as houseflies, mosquitoes and body lice. It was used for controlling malaria and typhus.

Exposure to high doses of DDT may cause vomiting, tremors or shakiness. Laboratory animal studies showed adverse effect of DDT on liver and reproduction. DDT is a persistent organic pollutant, readily absorbed in soils and tends to accumulate in the ecosystem. When dissolved in oil or other liquid, it is readily absorbed by the skin. It is resistant to metabolism. It accumulates in fatty tissues. There is a ban on use of DDT due to all these adverse effects .



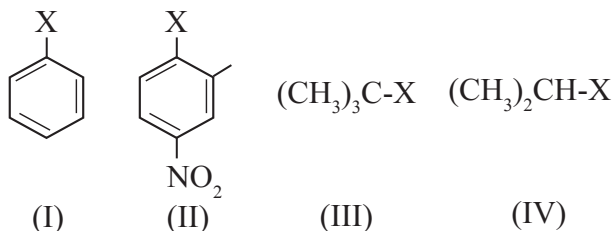
#### Do you know ?


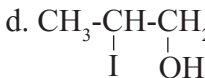
DDT, the first chlorinated organic insecticides, was originally prepared in 1873, but it was not until 1939 that Paul Muller of Geigy Pharmaceuticals in Switzerland discovered the effectiveness of DDT as an insecticide. Paul Muller was awarded the Nobel Prize in Medicine and Physiology in 1948 for this discovery. The use of DDT increased enormously on a worldwide basis after World War II, primarily because of its effectiveness against the mosquito that spreads malaria and lice that carry typhus. Many species of insects developed resistance to DDT, and it was also discovered to have a high toxicity towards fish. DDT is not metabolised very rapidly by animals; instead, it is deposited and stored in the fatty tissues. The use of DDT was banned in the United States in 1973, although it is still in use in some other parts of the world.

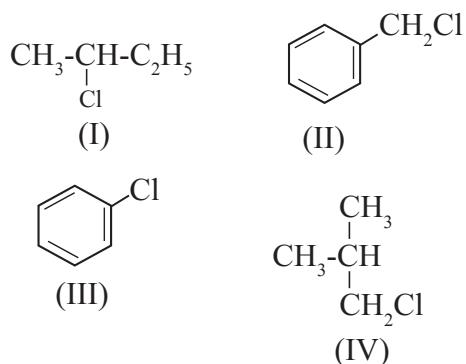
## Exercises

### 1. Choose the most correct option.

- i. The correct order of increasing reactivity of C-X bond towards nucleophile in the following compounds is

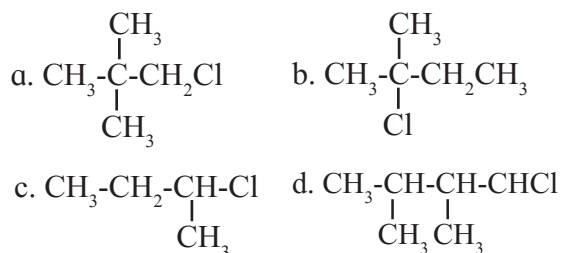


- a. I < II < III < IV  
 b. II < I < III < IV  
 c. III < IV < II < I  
 d. IV < III < I < II
- ii.  $\text{CH}_3\text{-CH=CH}_2 \xrightarrow[\text{peroxide}]{\text{HI}}$
- The major product of the above reaction is,
- a. I-CH<sub>2</sub>-CH=CH<sub>2</sub>      b. CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>I  
 c.       d. 
- iii. Which of the following is likely to undergo racemization during alkaline hydrolysis ?



- a. Only I                      b. Only II  
 c. II and IV                d. Only IV

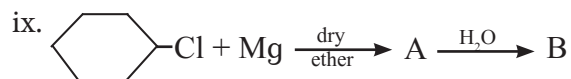
- iv. The best method for preparation of alkyl fluorides is
- a. Finkelstein reaction  
 b. Swartz reaction  
 c. Free radical fluorination  
 d. Sandmeyer's reaction
- v. Identify the chiral molecule from the following.
- a. 1-Bromobutane  
 b. 1,1- Dibromobutane  
 c. 2,3- Dibromobutane  
 d. 2-Bromobutane
- vi. An alkyl chloride on Wurtz reaction gives 2,2,5,5-tetramethylhexane. The same alkyl chloride on reduction with zinc-copper couple in alcohol give hydrocarbon with molecular formula C<sub>5</sub>H<sub>12</sub>. What is the structure of alkyl chloride



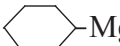
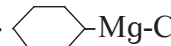
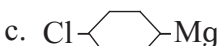
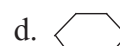
- vii. Butanenitrile may be prepared by heating
- a. propanol with KCN  
 b. butanol with KCN  
 c. n-butyl chloride with KCN  
 d. n-propyl chloride with KCN

viii. Choose the compound from the following that will react fastest by  $S_N1$  mechanism.

- 1-iodobutane
- 1-iodopropane
- 2-iodo-2 methylbutane
- 2-iodo-3-methylbutane



The product 'B' in the above reaction sequence is,

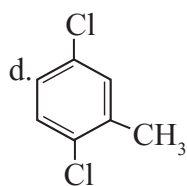
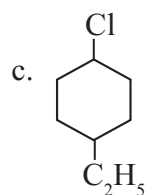
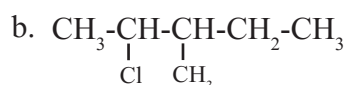
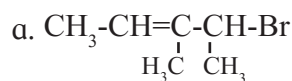
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x. Which of the following is used as source of dichlorocarbene

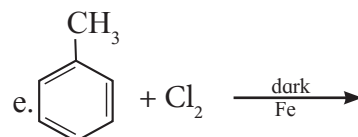
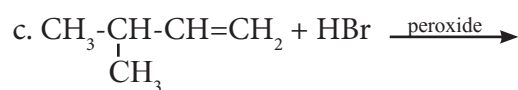
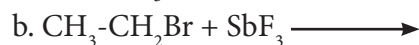
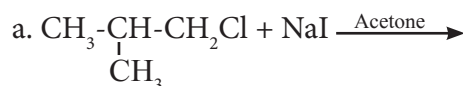
- tetrachloromethane
- chloroform
- iodoform
- DDT

## 2. Do as directed.

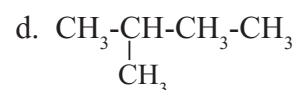
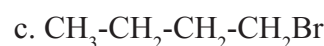
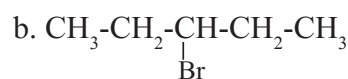
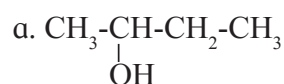
i. Write IUPAC name of the following compounds



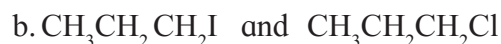
ii. Write structure and IUPAC name of the major product in each of the following reaction.



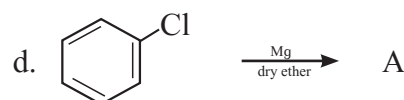
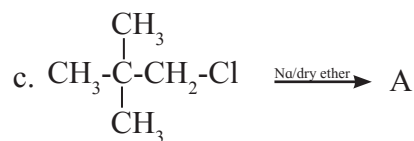
iii. Identify chiral molecule/s from the following.



iv. Which one compound from the following pairs would undergo  $S_N2$  faster from the?



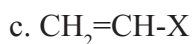
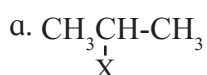
v. Complete the following reactions giving major product.





- vi. Name the reagent used to bring about the following conversions.
- Bromoethane to ethoxyethane
  - 1-Chloropropane to 1 nitropropane
  - Ethyl bromide to ethyl isocyanide
  - Chlorobenzene to biphenyl
- vii. Arrange the following in the increase order of boiling points
- 1-Bromopropane
  - 2- Bromopropane
  - 1- Bromobutane
  - 1-Bromo-2-methylpropane
- viii. Match the pairs.

#### Column I



#### Column II

i. vinyl halide

ii. alkyl halide

iii. allyl halide

iv. benzyl halide

v. aryl halide

### 3. Give reasons

- Haloarenes are less reactive than halo alkanes.
- Alkyl halides though polar are immiscible with water.
- Reactions involving Grignard reagent must be carried out under anhydrous condition.
- Alkyl halides are generally not prepared by free radical halogenation of alkanes.

4. Distinguish between  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  mechanism of substitution reaction ?

5. Explain - Optical isomerism in 2-chlorobutane.

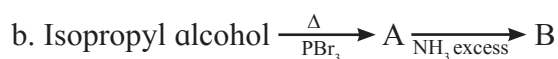
6. Convert the following.

- Propene to propan-1-ol
- Benzyl alcohol to benzyl cyanide
- Ethanol to propane nitrile

- But-1-ene to n-butyl iodide
- 2-Chloropropane to propan-1-ol
- tert-Butyl bromide to isobutyl bromide
- p-Nitrochlorobenzene to p-nitrophenol
- Propene to 1-nitropropane

### 7. Answer the following

- HCl is added to a hydrocarbon 'A' ( $\text{C}_4\text{H}_8$ ) to give a compound 'B' which on hydrolysis with aqueous alkali forms tertiary alcohol 'C' ( $\text{C}_4\text{H}_{10}\text{O}$ ). Identify 'A', 'B' and 'C'.
- Complete the following reaction sequences by writing the structural formulae of the organic compounds 'A', 'B' and 'C'.



- Observe the following and answer the questions given below.



- Name the type of halogen derivative
- Comment on the bond length of C-X bond in it
- Can react by  $\text{S}_{\text{N}}1$  mechanism? Justify your answer.

#### Activity :

- Collect detailed information about Freons and their uses.
- Collect information about DDT as a persistent pesticide.

#### Reference books

- Organic chemistry by Morrison, Boyd, Bhattacharjee, 7<sup>th</sup> edition, Pearson
- Organic chemistry by Finar, Vol 1, 6<sup>th</sup> edition, Pearson

