



25



313en25

COMPOUNDS OF CARBON CONTAINING HALOGENS (HALOALKANES AND HALOARENES)

You have studied about the hydrocarbons in the previous lesson. When a hydrogen attached to a carbon atom in the hydrocarbons is replaced by a halogen atom (i.e. F, Cl, Br or I), the compounds formed are called **haloalkanes or haloarenes**. The halogen derivatives do not occur in nature and they are synthesized in the laboratory. These compounds have wide applications in industry and domestic uses. They are used as industrial solvents, in the manufacture of pharmaceuticals, as dry cleaning agents, as pesticides, as anesthetics in medicine, as refrigerants, as fire extinguishers and as antiseptics. In this lesson, you will study the nomenclature, methods of preparation and properties of this important class of carbon compounds.



OBJECTIVES

After reading this lesson, you will be able to :

- define haloalkanes and haloarenes;
- name haloalkanes and haloarenes according to IUPAC rules;
- explain methods of preparation, physical properties, chemical properties and uses of haloalkanes and haloarenes;
- distinguish between haloalkanes and haloarenes, and
- explain the preparation, properties and uses of some important polyhalogen compounds.

MODULE - 7

Chemistry of Organic Compounds



Notes

Compounds of Carbon Containing Halogens (Haloalkanes and Haloarenes)

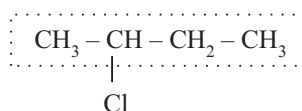
25.1 NOMENCLATURE OF HALOALKANES AND HALOARENES

You have learnt the nomenclature of hydrocarbons in lesson 25. In this section, you will learn the nomenclature of halogen derivatives of both aliphatic and aromatic hydrocarbons i.e. haloalkanes and haloarenes.

Nomenclature of Haloalkanes

The following rules are used for naming haloalkanes according to the IUPAC system.

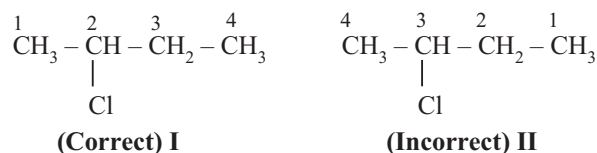
1. The longest chain of the carbon atoms bearing the halogen atom is selected.



The longest chain of carbon atoms in the above example is shown in the box.

2. Numbering of the carbon atoms in the chain is done in such a way that the carbon atom bearing the halogen atom gets the lowest number.

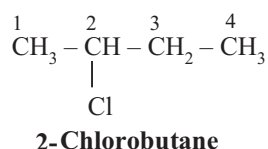
For example.



In the above example, numbering shown in (I) is correct while in (II), it is incorrect since the carbon atom bearing halogen atom gets lower number in I than in II.

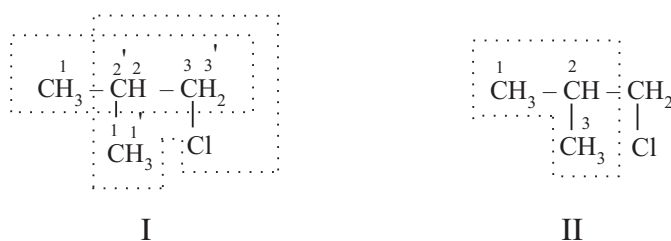
3. The word chloro, is prefixed to the parent hydrocarbon name.

So, the correct name for the above halocompound is



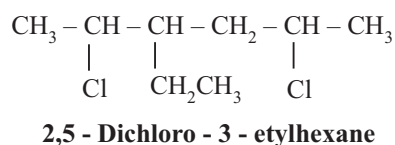
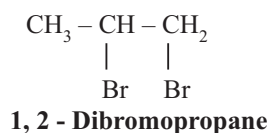
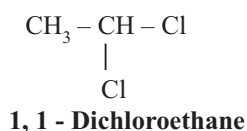
4. In case of alkyl substituted haloalkanes, the longest chain containing halogen atom is selected for numbering.

For example :



In structure I, the selection of chain is shown by two different ways. Both the ways of selection are correct since they include chloro group. In structure II numbering shown is not correct since it does not include chloro group.

5. When two or more halogen atoms are present in a compound, the longest chain selected must contain the maximum number of halogen atoms. The multiplicative prefixes (*di*, *tri*, *tetra*, etc.) are added before the name of halogen atom to indicate the number of halogen atoms. The following examples illustrate this rule.



Some more examples are given in Table 25.1 to illustrate the above rules.

Table 25.1: Names of Some Haloalkanes

Compound	IUPAC name	Common name
$\text{CH}_3\text{CH}_2\text{Br}$	Bromoethane	Ethyl bromide
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$	1-Bromopropane	<i>n</i> -Propyl bromide
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{Br} \end{array}$	2-Bromopropane	<i>iso</i> -Propyl bromide
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{Cl} \\ \\ \text{CH}_3 \end{array}$	1-Chloro-2-methylpropane	<i>iso</i> -Butyl chloride



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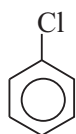
Compounds of Carbon Containing Halogens (Haloalkanes and Haloarenes)

$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ \\ \text{Cl} \end{array}$	2-Chlorobutane	<i>sec</i> -Butyl chloride
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{Cl} \end{array}$	2-Chloro-2-methylpropane	<i>tert</i> -Butyl chloride

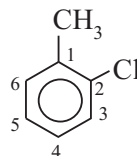
* All compounds essentially do not have common names.

Nomenclature of Haloarenes

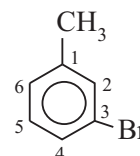
Haloarenes are those aromatic halogen compounds in which the halogen atom is directly linked to an aromatic ring. Their general formula is Ar-X where Ar represents an aromatic ring and X denotes the halogen. In naming a haloarene, the prefix *chloro*, *bromo*- or *iodo*- etc. is added to name of arene according to halogen(s) present. The relative positions of halogen atoms are indicated by appropriate numbers. The prefixes *ortho* (*o*-), *meta* (*m*-) and *para* (*p*-) are also commonly used respectively to indicate the relative positions i.e. 1,2- ; 1,3- and 1,4- of substituents in a benzene ring. Following examples illustrate the nomenclature of some haloarenes.



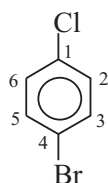
Chlorobenzene



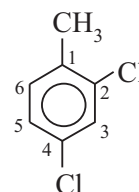
2-Chlorotoluene
(*o*-Chlorotoluene)



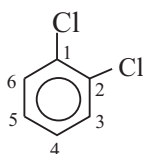
3-Bromotoluene
(*m*-Bromotoluene)



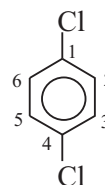
4-Bromochlorobenzene
(*p*-bromochlorobenzene)



2, 4-Dichlorotoluene



1, 2-Dichlorobenzene
(*o*-Dichlorobenzene)

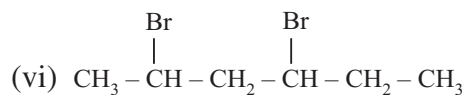
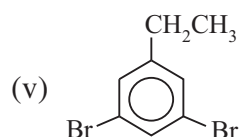
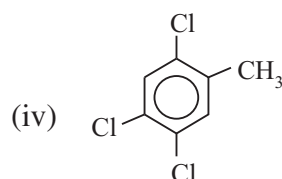
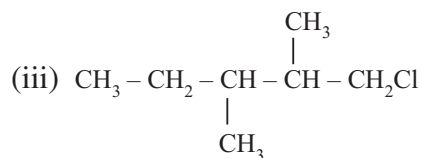
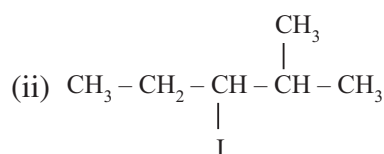
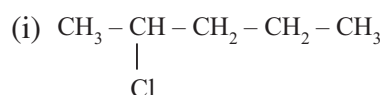


1, 4-Dichlorobenzene
(*p*-Dichlorobenzene)



INTEXT QUESTIONS 25.1

1. Write the IUPAC names of each of the following compounds :



2. Draw structural formulae of the following compounds:

(i) 2-Bromo-3-methylbutane

(ii) 3-Chloro-4-methylhexane

(iii) 3-Bromochlorobenzene

(iv) 2,4-Dibromotoluene



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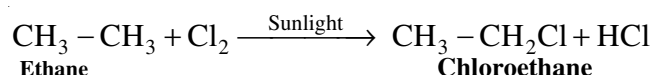
Notes

Compounds of Carbon Containing Halogens (Haloalkanes and Haloarenes)

25.2 PREPARATION OF HALOALKANES AND HALOARENES

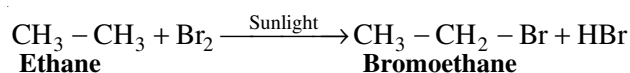
25.2.1 Preparation of Haloalkanes

- (i) **From Hydrocarbons :** Direct halogenation of hydrocarbons takes place in the presence of sunlight or at high temperature in dark. For example, chloroethane is prepared by monochlorination of ethane.



This reaction follows a free radical mechanism. You have already learnt the mechanism of chlorination of methane in lesson 26.

Bromo derivatives of alkanes are also prepared by direct bromination.

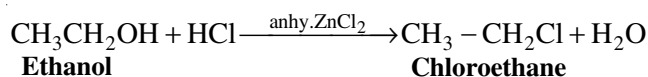


Direct iodination is not possible with iodine as the reaction is reversible. Direct fluorination is also not possible because due to the high reactivity of the fluorine, the reaction cannot be controlled.

- (ii) **From Alcohols :** Alcohols are converted into haloalkanes by treating with (a) hydrogen halides (b) phosphorus halides or (c) thionyl chloride.

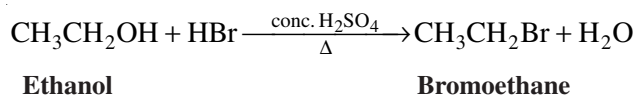
- (a) **Reaction with Hydrogen Halides :** Hydrogen halides react with an alcohol in presence of a dehydrating agent such as anhydrous zinc chloride to produce a haloalkane.

Chloroethane is conveniently prepared by the reaction of ethanol with concentrated hydrochloric acid in presence of anhydrous zinc chloride.



Zinc chloride absorbs water from the reaction mixture and thus prevents the reverse reaction.

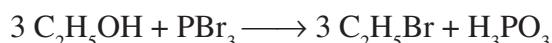
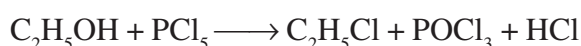
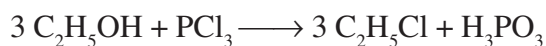
Bromoethane is obtained by refluxing ethanol with HBr in presence of little concentrated H_2SO_4 as the catalyst.



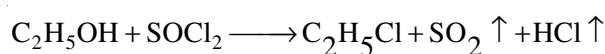


Notes

- (b) **Reaction with Phosphorus Halides :** Haloalkanes are conveniently prepared by the reaction of an alcohol with a phosphorus halide (PCl_3 , PCl_5 or PBr_3) according to the following equations.



- (c) **Reaction with Thionyl Chloride :** Thionyl chloride (SOCl_2) is another reagent which reacts with an alcohol to yield a chloroalkane.



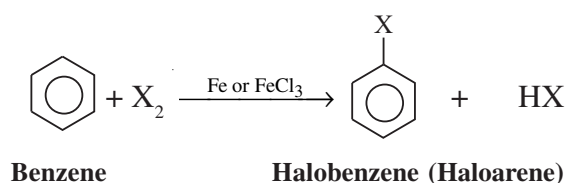
Ethanol

Chloroethane

As both the byproducts, SO_2 and HCl are gases, the purification of final product is not required.

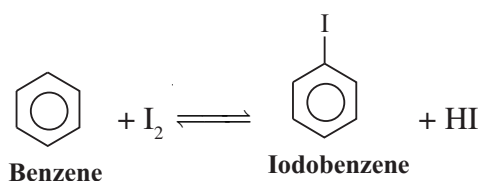
25.2.2 Preparation of Haloarenes

- (i) **From Aromatic Hydrocarbons :** Haloarenes are obtained by direct halogenation of aromatic hydrocarbons in the presence of a catalyst. Usually iron filings or iron (III) halide is used as the catalyst.

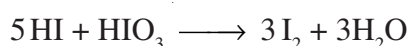


where $\text{X} = \text{Cl}$ or Br

The direct iodination of aromatic hydrocarbons is not a useful reaction since the HI produced reduces the aryl iodide back to the aromatic hydrocarbon.



However, in the presence of an oxidizing agent such as nitric acid, iodic acid (HIO_3), mercury oxide, the HI produced is either oxidized to iodine or is eliminated as mercuric iodide and, thus, iodobenzene is obtained.



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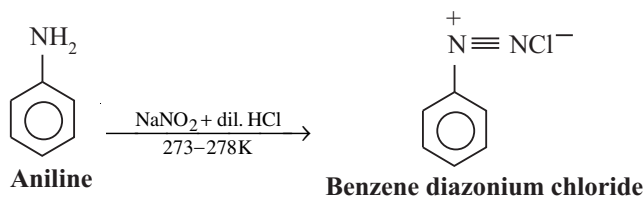


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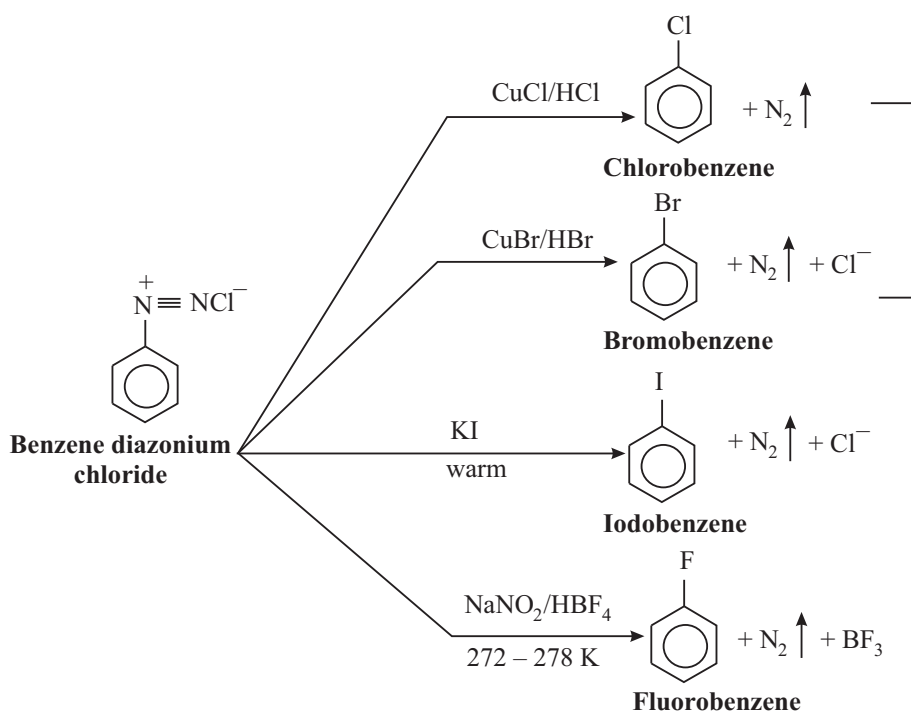
Fluorobenzene cannot be prepared by direct fluorination of aromatic hydrocarbons since the reaction is very violent and cannot be controlled.

- (ii) **From Diazonium Salts** : Benzene diazonium salt is formed by treating an aromatic primary amine with NaNO_2 and dil. HCl at low temperature. The process is known as **diazotisation**.

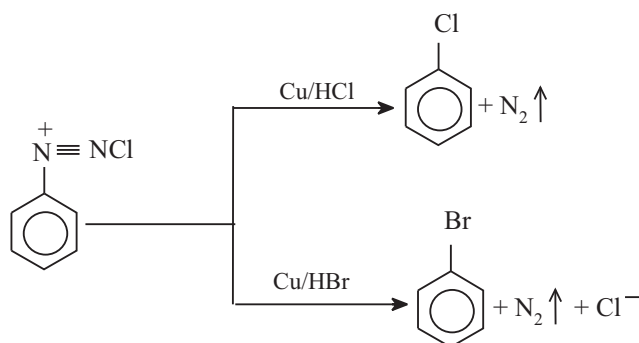


Diazonium salts are highly reactive compounds. They are used in the preparation of a large number of arene derivatives. When a diazonium salt is treated with copper (I) chloride (Cu_2Cl_2) or copper (I) bromide (Cu_2Br_2), the corresponding haloarene is formed.

This reaction is known as **Sandmeyer reaction**. It is used for introducing a chloro or bromo group in the benzene ring.



Haloarenes can also be prepared by reacting benzene diazonium chloride with copper powder in presence of corresponding halogen acid. This reaction is called **Gattermann reaction** and is shown below :

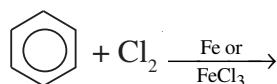


Notes



INTEXT QUESTIONS 25.2

1. Write the structure of the main product obtained by treating 1-propanol with excess of hydrogen chloride in the presence of anhydrous zinc chloride.
2. What will be the product obtained on treatment of 1-propanol with thionyl chloride?
3. Give one example of preparation of chlorobenzene using Sandmeyer reaction?
4. Complete the following reaction :

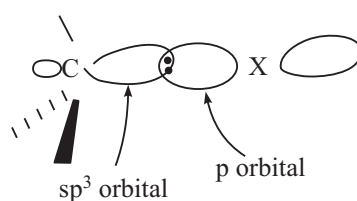


25.3 PROPERTIES OF HALOALKANES AND HALOARENES

Before we discuss the important physical and chemical properties of alkylhalides and aryl halides, let us consider the nature of C—X bond.

25.3.1 The Nature of C—X Bond

In alkyl halides, the carbon – halogen bond is formed by the overlap of the sp^3 hybrid orbital of carbon atom with the p -orbital of the halogen atom.



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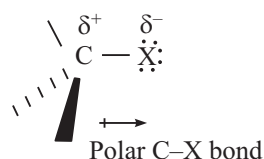


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As one moves from fluorine to iodine, the size of the halogen atom increases and hence the overlap decreases. Hence, the C–X bond becomes longer and weaker on going from alkyl fluorides to alkyl iodides.

Also, the halogens are more electronegative than carbon. Thus, the electron density along the C–X bond is displaced in the direction of the halogen. Thus, the C–X bond is polar in nature. The carbon atom bears a partial positive charge (δ^+) and the halogen atom bears a partial negative charge (δ^-).

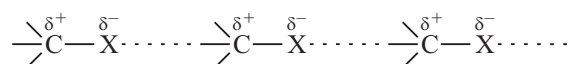


You will now study that this bond polarity has important impact on the physical and chemical properties of alkyl halides.

The partially positively charged carbon in haloalkanes can be easily attacked by anions and electron rich species which are called *nucleophiles*. On the other hand, the partially negatively charged halogen atom can be attacked by the cations and electron deficient species.

25.3.2 Physical Properties

1. The lower alkyl halides (CH_3F , CH_3Cl , CH_3Br , $\text{C}_2\text{H}_5\text{Cl}$) are gases at room temperature. The other alkyl halides containing upto C_{18} are liquids having high boiling points.
2. Haloalkanes and haloarenes are moderately polar molecules ($\text{>C}^{\delta+}-\text{X}^{\delta-}$). Still they are immiscible in water. It is due to their inability to form hydrogen bonds with water molecules.
3. The melting and boiling points of haloalkanes and haloarenes are higher than those of their parent hydrocarbons (Table 25.2) This is due to (i) the greater molecular mass and hence greater magnitude of van der Waals forces of attraction in halocompounds than in the parent hydrocarbons and (ii) the existence of intermolecular dipole-dipole interaction, as shown below:

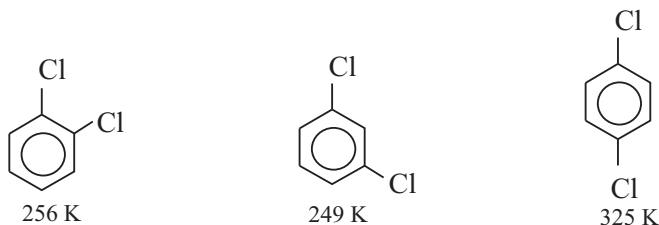


For a given alkyl or aryl group, the boiling points increase from fluoro to iodo compounds as the size of halogen atom increases. The boiling points of halomethanes, haloethanes and halobenzene given in the Table 25.2 to show this variation.

Table 25.2 : Boiling Points of Haloalkanes and Haloarenes

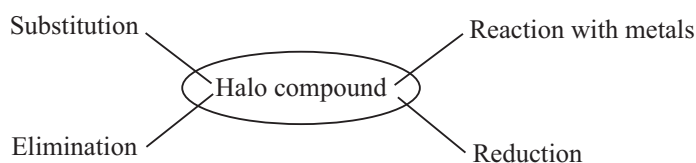
Compound	Boiling Point (K)				
	X=H	X=F	X=Cl	X=Br	X=I
CH ₃ - X	111.5	194.6	248.8	276.6	315.4
C ₂ H ₅ - X	184.3	241	285	311.4	345
C ₆ H ₅ - X	351	358	405	429	461

4. All monohalobenzenes are liquids at room temperature. Among dihalobenzenes, the *para* isomers have the highest melting points. It is due to the greater symmetry that causes a better packing of molecule in the *para* isomer.

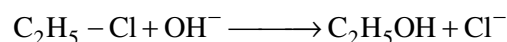


25.3.4 Chemical Properties

Halo compounds can undergo the following types of reactions :



1. Substitution : Substitution reactions are those in which an atom or a group of atoms from the reactant molecule is displaced by another atom or a group of atoms. For example, on treating chloroethane with sodium hydroxide, the chlorine atom of chloroethane is substituted by the hydroxyl group and ethanol is formed as the reaction product.



In this reaction, it is to be noted that the hydroxide ion (nucleophile) displaces the chlorine atom from C₂H₅Cl as chloride ion (another nucleophile). Such reactions which are initiated by the attack of a nucleophile are known as **nucleophilic reactions**. In haloalkanes, the carbon atom carrying the halogen atom is electron deficient due to -I effect of halogen atom. This electron deficient carbon atom is susceptible to attack by a nucleophile. Thus, you may conclude that haloalkanes



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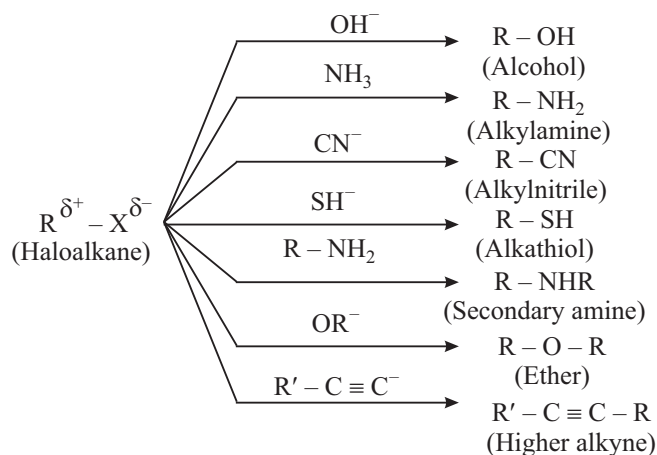
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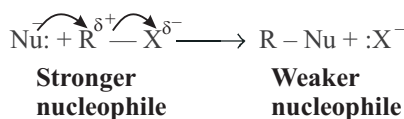
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undergo **nucleophilic substitution reactions**. Following are a few examples of nucleophilic substitution reactions of haloalkanes.



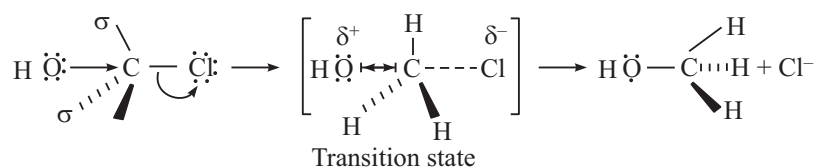
In all the above reactions, the stronger nucleophile (HO^- , $C_2H_5O^-$, CN^- or NH_3 etc.) displaces a weaker nucleophile X^- as



25.3.3 Mechanism of Nucleophilic Substitution Reactions

The nucleophilic substitution reactions could be either S_N1 or S_N2 type.

When the nucleophile attacks the haloalkane, and simultaneously the leaving group leaves then, the reaction is called **nucleophilic substitution bimolecular** i.e. S_N2 .



Also, note that it is a one step process and the transition state involves *two* species. The formation of this transition state is the rate determining step in this mechanism.

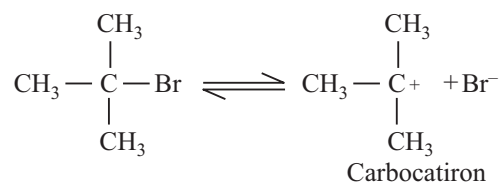
Here, the bond making and the bond breaking takes place simultaneously. The nucleophile (OH^-) attacks from one side of the carbon atom whereas the leaving group (Cl^-) leaves from the opposite direction. Hence, there is an *inversion* of configuration at the carbon atom.



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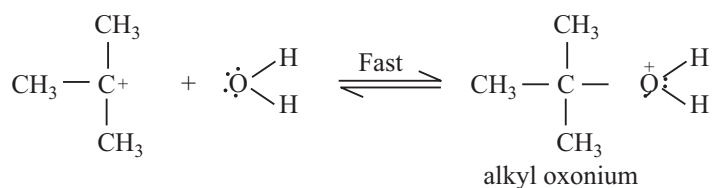
Primary alkyl halides undergo substitution by S_N2 mechanism.

However, in case of tertiary alkyl halides, the substitution takes place by an alternative mechanism, i.e. *substitution nucleophilic*, unimolecular or S_N1 mechanism. For example, in the hydrolysis of 2-bromo-2-methylpropane, any one molecule participates in the rate determining step which is the dissociation of the alkyl halide to alkyl cation and bromide ion.

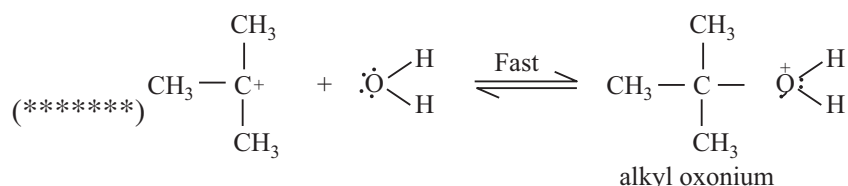


This alkyl cation is a carbocation and its formation is a slow and rate determining step.

After this, as soon as this carbocation is formed, the nucleophile, which is water (solvent) molecule, attacks on it which is a fast step.



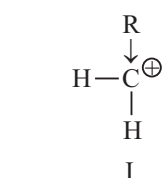
Finally, the alkyl oxonium ion loses a proton to give the alcohol as the product.



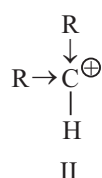
Since, the S_N1 reactions proceed via the formation of carbocations, the stability of the carbocation formed is an important factor in the S_N1 reactions.

Stability of Carbocations

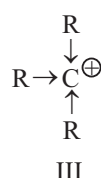
Let us consider the following carbocations.



A primary carbocation



A secondary carbocation



A tertiary carbocation

MODULE - 7

Chemistry of Organic Compounds



Notes

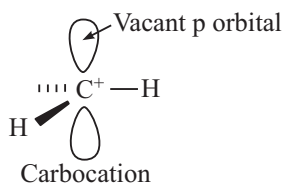
Compounds of Carbon Containing Halogens (Haloalkanes and Haloarenes)

A carbocation is classified as *primary*, *secondary* or *tertiary* depending upon whether the positively charged carbon atom is linked to *one*, *two* or *three* carbon atoms, respectively.

Here, as the *number of alkyl groups* attached to the positively charged carbon atoms increases, the stability of the carbocation *also increases*. This is because alkyl groups are electron releasing in nature and help in the stabilization of the positive charge on the carbon atom of the carbonation.

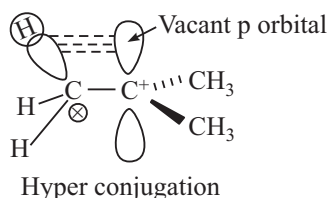
Thus, a tertiary carbocation is more stable than a secondary carbocation which, in turn, is more stable than a primary carbonation.

The above order of stability of carbocations is also explained on the basis of **hyperconjugation**. Hyperconjugation results from the overlap of a *p* orbital with a neighbouring bonding molecular orbital. In a carbocation, the *p* orbital on the carbon carrying positive charge is vacant.



This vacant *p* orbital can overlap with the neighboring orbital of C–H bond and stabilize the charge. The more the number of such neighboring orbitals, the more will be the stabilization.

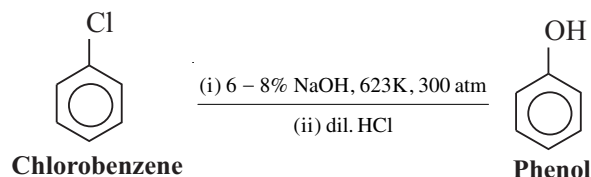
If we see the extent of hyper conjugation possible in primary, secondary and tertiary carbocation we can observe that in a primary carbocation cation 3 C–H bonds are available for hyperconjugation and in secondary carbocation 6 C–H bonds are available for hyperconjugation. Similarly, in a tertiary carbocation, 9 C–H bonds are available for hyperconjugation.



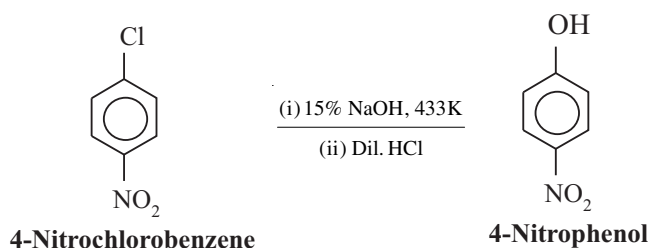
Hence, a tertiary carbocation is more stable than a secondary carbocation which is, in turn, more stable than a primary carbocation.

Thus, this also explains why tertiary halides undergo nucleophilic substitution reactions by S_N1 mechanism.

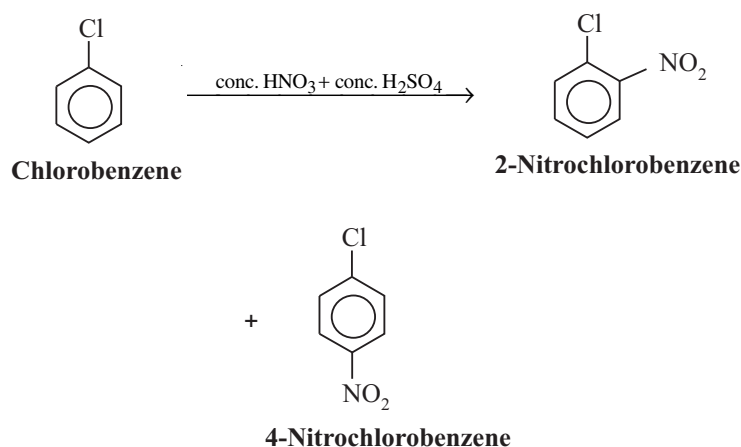
Haloarenes are almost unreactive to reagents such as NaOH, C_2H_5ONa , NaCN and NH_3 under ordinary laboratory conditions but can show nucleophilic substitution reactions under drastic conditions.



It is also observed that the presence of electron withdrawing groups such as $-NO_2$ groups at *o*- and *p*-position (but not a *m*-position) with respect to halogen activates the halogens towards nucleophilic displacement. For example:



Haloarenes can also readily undergo substitution reactions in benzene ring. The benzene ring is an electron rich species. Therefore, it is attacked by an electron deficient species such as NO_2^+ . As *ortho* and *para* positions in haloarenes are electron rich due to resonance (Fig. 25.1), the electrophilic substitution takes place mainly at these positions. For example, the nitration of chlorobenzene, with a mixture of concentrated HNO_3 and H_2SO_4 , gives a mixture of 2-nitrochlorobenzene and 4-nitrochlorobenzene.



Haloalkanes are highly reactive compounds due to the presence of a polar carbon-halogen bond in their molecules. The bond energy values of C-X bonds in haloalkanes and haloarenes are given in Table 25.3.



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Chemistry of Organic Compounds



Notes

Compounds of Carbon Containing Halogens (Haloalkanes and Haloarenes)

Table 25.3 : C-X bond energy Values

Bond	Bond Energy/kJ mol ⁻¹
C-F	485
C-Cl	339
C-Br	284
C-I	213

These bond energy values show that C-I bond is the weakest bond and C-F bond is the strongest bond. Therefore, the order of reactivity of haloalkanes is iodoalkane > bromoalkane > chloroalkane > fluoroalkane.

Comparing the haloalkanes and haloarenes, haloalkanes are found to be more reactive than haloarenes in reactions involving the breaking of C-X bond (X = F, Cl, Br, or I). It is due to the existence of the phenomenon of resonance which causes the carbon-halogen bond to acquire double bond character in haloarenes. The resonating structures of chlorobenzene are shown below :

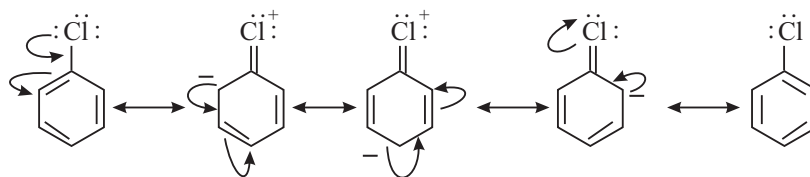
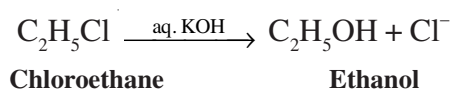
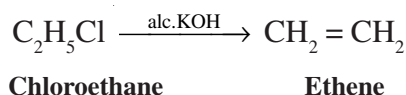


Fig. 25.1 : Resonance Structures of Chlorobenzene

2. Elimination reactions : When haloalkanes are heated with aqueous solution of potassium or sodium hydroxide, the major product formed is the alcohol, produced by nucleophilic displacement of the halogen atom by HO⁻.



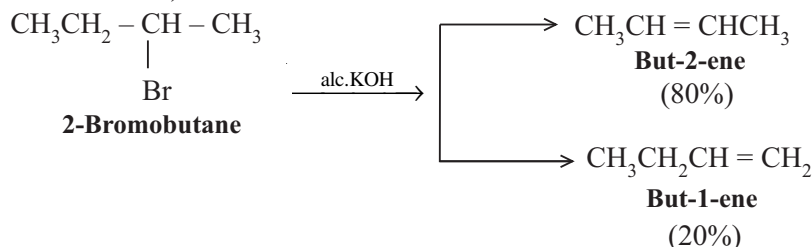
If a haloalkane is heated with concentrated alcoholic potassium hydroxide, the major product formed is an alkene due to the elimination of hydrogen halide. This is called β -elimination or dehydrohalogenation.



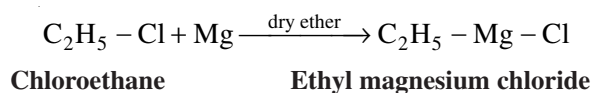
In this reaction, the OH⁻ ion acts as a base and removes a proton from the molecule.

If the structure of alkyl halide is such that it can undergo elimination in two different ways, then the more highly substituted alkene (i.e. having lesser number of hydrogen atoms on the doubly bonded carbon atoms) is the major product of elimination. This is known as **Saytzeff's rule**. For example, elimination reaction

of 2-bromobutane gives 2-butene as major product according to the Saytzeff's rule, (refer lesson 26).

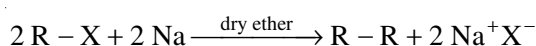


3. Reactions with metals : Haloalkanes and haloarenes react with a variety of metals (zinc, magnesium and lithium). The compounds so obtained have a metal atom directly bonded to a carbon atom. Such compounds in which the metal atom is directly bonded to a carbon atom are known as **organometallic compounds**. The organometallic compounds of magnesium with alkyl and aryl halides are known as **Grignard reagents**.

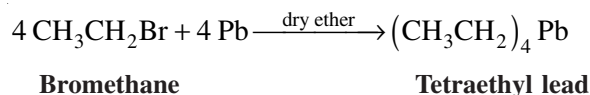


These are named after the French chemist Victor Grignard.

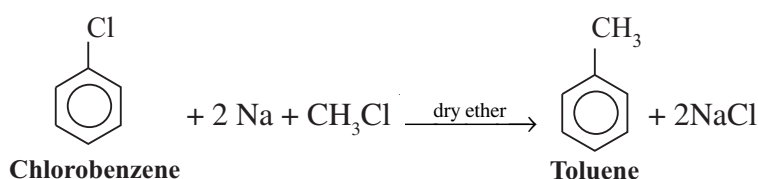
Alkyl halides react with metallic sodium in presence of dry ether to form symmetrical higher alkanes. This reaction is called **Wurtz reaction**.



Ethyl bromide can react with lead in presence of dry ether to form tetraethyl lead (TEL) which is used as antiknocking agent in gasoline used for running automobiles.



When haloarenes react with alkyl halides in presence of sodium and dry ether, the alkyl derivatives of benzene are formed. This reaction is called **Wurtz-Fittig reaction**.



French Chemist

Victor Grignard was awarded Nobel Prize in 1912. He introduced **organomagnesium halide as a common synthetic reagent**.



Notes

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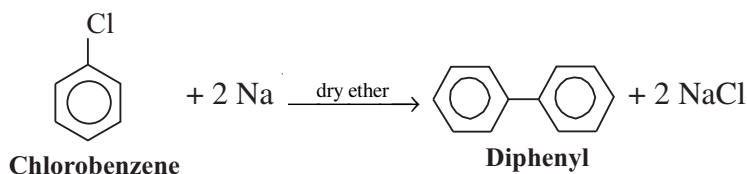
Chemistry of Organic Compounds



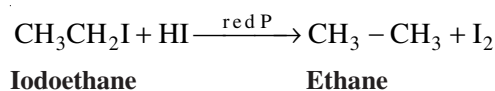
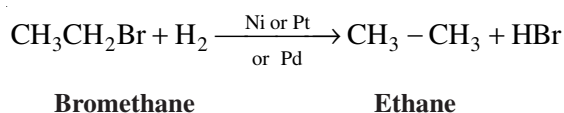
Notes

Compounds of Carbon Containing Halogens (Haloalkanes and Haloarenes)

When haloarenes are treated with sodium, diaryls are produced. This reaction is called **Fittig reaction**.

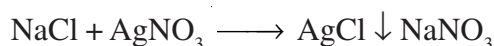
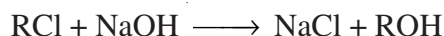


4. Reduction : Haloalkanes can be reduced to the corresponding alkanes. For example, bromoethane can be reduced to ethane by using metal catalyst such as nickel or palladium or platinum or by using hydroiodic acid (HI) in presence of red phosphorus.



Distinction between haloalkanes and haloarene

Haloalkane and haloarenes can be distinguished by silver nitrate (AgNO_3). Haloalkanes react with AgNO_3 to give white precipitate of AgCl while haloarenes do not react.



INTEXT QUESTIONS 25.3

1. Although haloalkanes are polar in nature, they are immiscible in water. Explain.
2. Which one of the following isomers has the higher boiling point and why?
(i) *o*-dichlorobenzene (ii) *p*-dichlorobenzene
3. What will be the products of nitration of chlorobenzene?
4. What products will be obtained when ethylbromide reacts with
(i) aq. KOH and (ii) alc. KOH
5. What is the major product of elimination reactions of 2-bromobutane?

25.4 SOME USEFUL POLY HALOGEN COMPOUNDS

A large number of polyhalogen aliphatic and aromatic halogen compounds are known. These are extensively used as solvents, pesticides, anaesthetics etc. Some of the important compounds are chloroform (CHCl_3), iodoform (CHI_3), carbon tetrachloride (CCl_4), benzene hexachloride (BHC), DDT, etc.

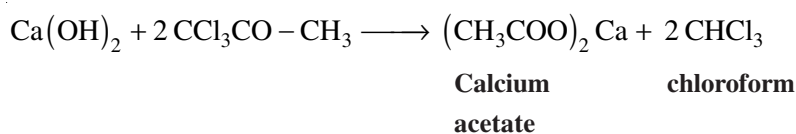
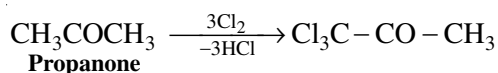
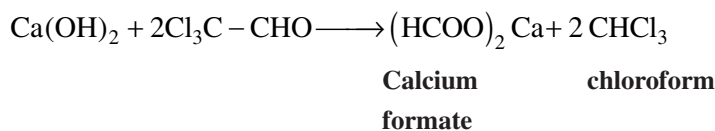
Let us now study some of these compounds.

25.4.1 Chloroform

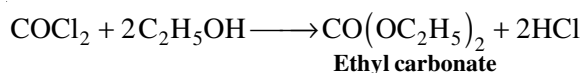
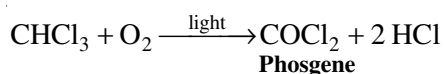
Chloroform is a derivative of the simplest hydrocarbon, methane. Its IUPAC name is trichloromethane.

1. From Ethanol

Chloroform is prepared in the laboratory by treating ethanol or propanone with chlorine gas in the presence of an alkali :



Chloroform is a colourless sweet smelling liquid (b.p. 334K). It is slowly oxidized by air in the presence of light to a poisonous gas, phosgene. Chemically phosgene is carbonyl chloride, (COCl_2). Therefore, chloroform is stored in dark coloured bottles to protect it from light. The bottles are completely filled so that the air is kept out. A small amount of ethanol is added to chloroform to convert toxic phosgene, if formed, into a nontoxic compound, ethyl carbonate.



Notes

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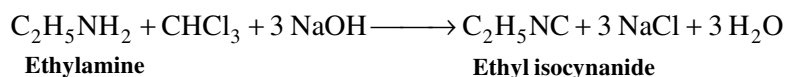
Chemistry of Organic Compounds



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Compounds of Carbon Containing Halogens (Haloalkanes and Haloarenes)

Chloroform is used in isocyanide test for the detection of primary amines. In this test, a mixture of amine and chloroform is heated with alcoholic NaOH. A foul smelling isocyanide is obtained. This test is also known as **carbylamine test**. It can be used to test aliphatic and aromatic primary amines.

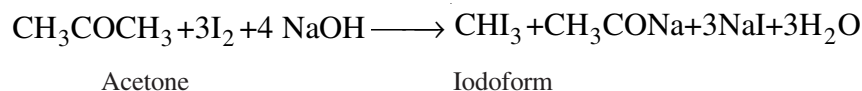
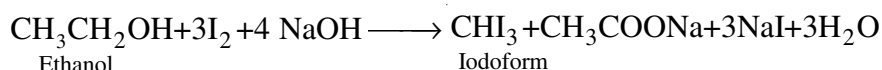


25.4.2 Iodoform

Iodoform is a pale yellow solid with a distinct smell. Its IUPAC name is triiodomethane.

Preparation

Iodoform is prepared by heating ethanol or acetone with iodine in the presence of alkali.

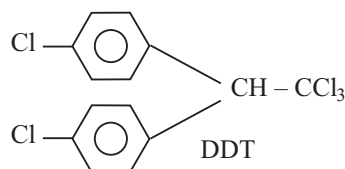


Yellow crystals of iodoform can easily be recognized by the characteristic smell. Formation of iodoform is used to test compounds containing $\text{CH}_3 - \text{C} = \text{O}$ or

$\text{CH}_3 - \underset{\text{OH}}{\text{CH}} -$ group. This test is known as **iodoform test**. Iodoform is used as an antiseptic.

25.4.3 Dichlorodiphenyltrichloroethane (DDT)

It is available in several different forms : powder, aerosols, granules, etc.



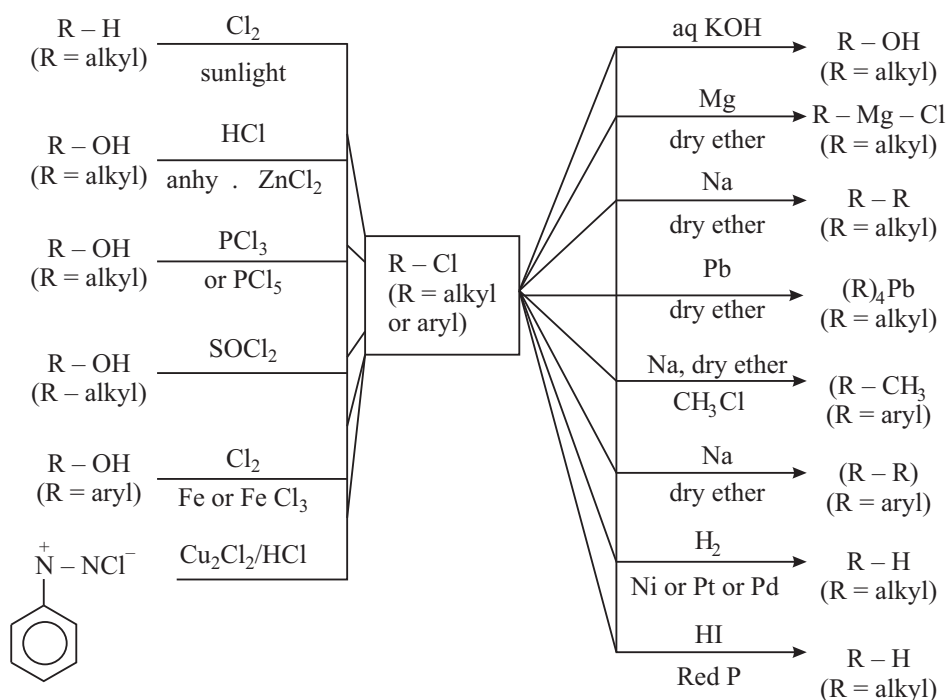
Uses : It is used mainly to control mosquito-borne malaria. It is also used as an agricultural insecticide. The use of DDT has been banned in many countries because being non-biodegradable, it accumulates in environment. It is toxic to other living organisms such as: mammals, birds, fishes, etc.


INTEXT QUESTIONS 25.4

1. Write IUPAC names of chloroform and iodoform.
2. Why is chloroform stored in dark coloured bottles?
3. What type of compounds will give a positive iodoform test?
4. Name two commonly used polyhalogen compounds.


WHAT YOU HAVE LEARNT

- Haloalkanes and haloarenes are important organic compounds having wide industrial and household applications.
- Various rules for IUPAC naming of haloalkanes and haloarenes.
- Methods of preparation and chemical properties of haloalkanes and haloarenes which are summarized below :



- Due to the polar nature, halo compounds have higher melting and boiling points than the corresponding hydrocarbons.
- Chemically, fluoro compounds are comparatively least reactive and iodo compounds are the most reactive. Also, haloalkanes are more reactive than haloarenes in reactions involving cleavage of C-X bond.


Notes

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Chemistry of Organic Compounds



Notes

Compounds of Carbon Containing Halogens (Haloalkanes and Haloarenes)

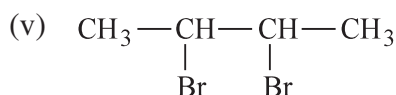
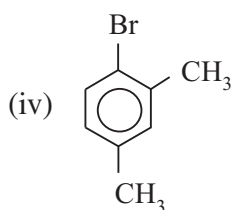
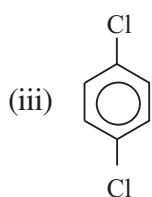
- Haloalkanes undergo nucleophilic substitution reactions. But in haloarenes, the substitution in the benzene ring is an electrophilic substitution reaction.
- Grignard reagents are produced by the reaction of a haloarene or haloalkane with magnesium metal.
- Chloroform and iodoform are useful trihalo derivatives of methane. Chloroform is prepared in the laboratory from ethanol or propanone by reacting with chlorine in presence of alkali.
- Iodoform test is given by compounds containing either $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{Oor}$ $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{Oor}$ $\text{CH}_3-\text{CH}-\text{OH}$ group.



TERMINAL EXERCISE

1. Give IUPAC names of the following compounds:

- sec*-butyl chloride
- iso*-propyl bromide



2. Name the product obtained by treating 2-propanol with hydrogen chloride in presence of anhydrous zinc chloride. Also write reaction involved.
3. Alkyl halides are more reactive towards nucleophilic reagents than aryl halides. Discuss briefly.
4. Write chemical equations for the reactions of :
 - (i) *n*-propanol with PCl_5 .
 - (ii) chlorine gas with benzene in presence of FeCl_3 as catalyst.

- (iii) bromoethane with aqueous KOH solution.
 - (iv) nitrous acid with aniline at 278 K.
 - (v) chlorobenzene with magnesium.
 - (vi) chlorobenzene with a mixture of conc. HNO_3 and H_2SO_4 .
5. Give reason for the following :
 - (i) Haloalkanes undergo nucleophilic substitution reactions.
 - (ii) Haloarenes undergo electrophilic substitution reactions.
 6. What is a Grignard reagent ? How is it prepared?
 7. Discuss briefly the following :
 - (i) Iodoform test
 - (ii) Carbylamine test
 - (iii) Diazotization
 - (iv) Relative reactivities of chloroethane and bromoethane
 8. How is chloroform prepared in the laboratory? Write the reaction for its preparation from ethanal.



ANSWERS TO INTEXT QUESTIONS

25.1

1.
 - (i) 2-Chloropentane
 - (ii) 3-Iodo-2-methylpentane
 - (iii) 1-Chloro-2,3-dimethylpentane
 - (iv) 1,3,4-Trichloro-6-methylbenzene or 2,4,5 - Trichlorotoluene
 - (v) 1,3-Dibromo-5-ethylbenzene
 - (vi) 2,4-Dibromohexane
2.
 - (i)

$$\begin{array}{cccc} \text{CH}_3 & - & \text{CH} & - & \text{CH} & - & \text{CH}_3 \\ & & | & & | & & \\ & & \text{CH}_3 & & \text{Br} & & \end{array}$$
 - (ii)

$$\begin{array}{ccccccc} \text{CH}_3 & - & \text{CH}_2 & - & \text{CH} & - & \text{CH} & - & \text{CH}_2\text{CH}_3 \\ & & & & | & & | & & \\ & & & & \text{Cl} & & \text{CH}_3 & & \end{array}$$



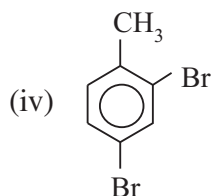
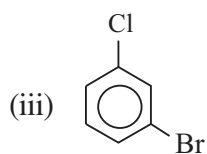
MODULE - 7

Chemistry of Organic Compounds



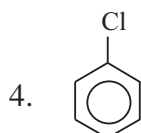
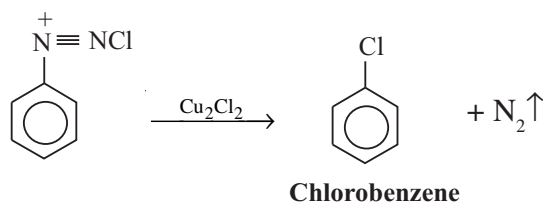
Notes

Compounds of Carbon Containing Halogens (Haloalkanes and Haloarenes)



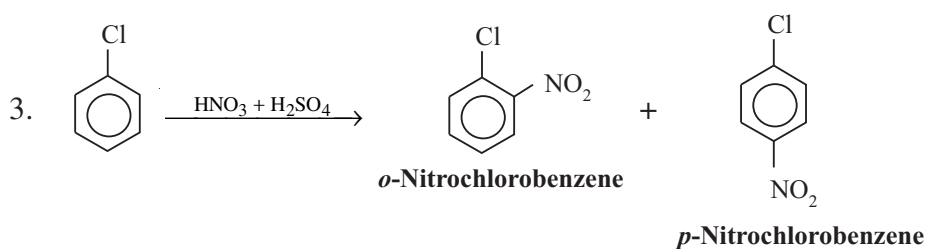
25.2

1. $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
2. 1-chloropropane
3. The Diazonium salt on treatment with copper (I) chloride Cu_2Cl_2 gives chlorobenzene.



25.3

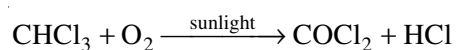
1. Due to their inability to form hydrogen bonds.
2. *Para* dichlorobenzene; due to greater symmetry and hence a better packing.



4. (i) $\text{C}_2\text{H}_5\text{Cl} \xrightarrow{\text{aq.KOH}} \text{C}_2\text{H}_5\text{OH}$
(ii) $\text{C}_2\text{H}_5\text{Cl} \xrightarrow{\text{alc.KOH}} \text{CH}_2 = \text{CH}_2$
5. $\text{CH}_3 - \text{CH}_2 - \underset{\text{Br}}{\text{CH}} - \text{CH}_3 \xrightarrow{\text{alc.KOH}} \text{CH}_3\text{CH} = \text{CHCH}_3$
major product

25.4

- (i) Trichloromethane
(ii) Triiodomethane
- Chloroform oxidises to phosgene in the presence of air and sunlight. Dark coloured bottles reduce formation of poisonous phosgene



- Compounds having $\text{CH}_3 - \underset{\text{|}}{\text{C}} = \text{O}$ or $\text{CH}_3 - \underset{\text{|}}{\text{CH}} -$ units in their structure.
OH

Dark coloured bottles reduce formation of poisonous phosgene.

- DDT, BHC, CHCl_3 and CHI_3 .

**Notes**