



ALKYL AND ARYL HALIDES

- * Halogen Derivatives
- * Polyhalogen Compounds
- * Ethyl Chloride
- * Aryl Halides

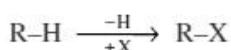
HALOGEN DERIVATIVES

Compounds derived from alkanes by the replacement of one or more hydrogen atoms by the corresponding number of halogen atoms are called halogen derivatives of alkanes or haloalkanes.

1.1.1

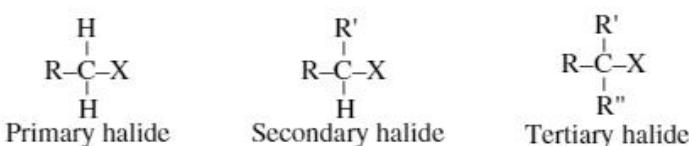
Classification Aliphatic halogen compounds

Monohalogen derivatives : Monohalogen derivatives of alkanes are called alkyl halides. They have the general formula RX, where R is an alkyl group and X is a halogen atom.



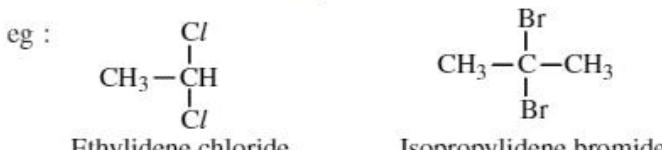
eg : CH₃Cl, C₂H₅Br, C₃H₇I, etc.

Alkyl halides are classified into primary, secondary or tertiary depending upon whether the halogen atom is attached to a primary, secondary or tertiary carbon atom respectively.

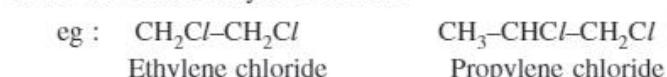


Dihalogen derivatives : Dihalogen derivatives of alkanes are derived by replacement of two hydrogen atoms by two halogen atoms. The dihalogen derivatives are mainly of three types.

Gem-halides : In these, both the halogen atoms are bonded to the same carbon atom. These are called alkylidene halides.



Vic-halides : In these, the halogen atoms are attached to adjacent carbon atoms. These are called alkylene halides.



Gem-dihalides
are alkylidene
halides

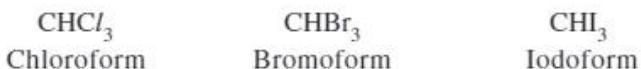
Vic-dihalides
are alkylene
halides

Terminal dihalides : In these, both the halogen atoms are bonded to the terminal carbon atoms. These are also called $\alpha-\omega$ halides or polymethylene halides.



Similarly if three or more hydrogen atoms are replaced by halogen atoms, they are called polyhalogen derivatives.

Trihalogen derivatives : Trihalogen derivatives of alkanes are derived by replacement of three hydrogen atoms by three halogen atoms. The trihalogen derivatives of methane are

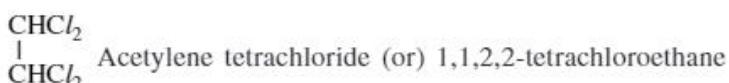


These compounds are termed as haloforms of the general formula, CHX_3 .

Tetrahalogen derivatives : Tetrahalogen derivatives of alkanes are derived by replacement of four hydrogen atoms by four halogen atoms.



The four halogen atoms may also be present on different carbon atoms.

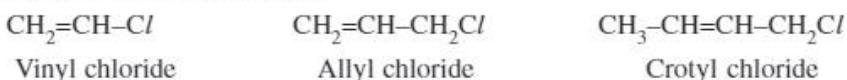


If all the hydrogen atoms in an alkane are replaced by halogen atoms, it is called per haloalkane.



Halogen derivatives of unsaturated hydrocarbons

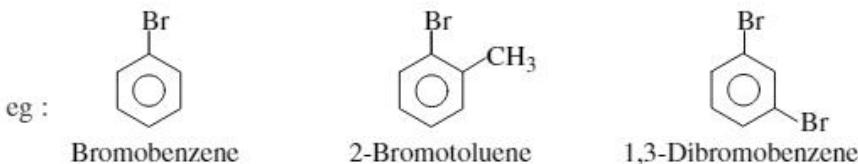
Replacement of some hydrogen atoms in alkenes or alkynes by some halogen atoms yields these compounds.



Aromatic halogen compounds

Halogen derivatives of aromatic compounds are of two types.

Aryl halides : In aryl halides, the halogen atom is directly linked to the carbon of benzene nucleus. These are also called nuclear substitution derivatives.

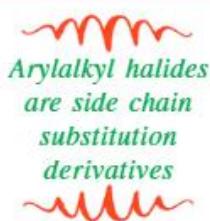


Arylalkyl halides : In arylalkyl halides, halogen atom is attached to the carbon atom of the side chain. These are also called side chain substitution derivatives. The side chain derivatives are very similar to aliphatic halogen derivatives.


Polyhalogen derivatives contain 3 or more halogen atoms

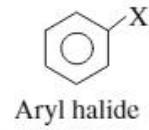
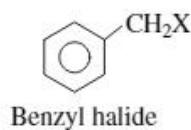
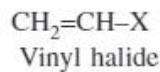
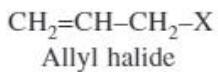
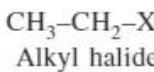


Aryl halides are nuclear substitution derivatives

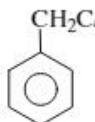


**Arylalkyl halides
are side chain
substitution
derivatives**

The halides in which halogen atom is attached to an sp^3 hybridized carbon atom next to a carbon-carbon double bond are known as allylic halides. The halides in which halogen atom is attached to the carbon atom of a carbon-carbon double bond are known as vinylic halides. The halides in which halogen atom is attached to a carbon atom next to aromatic ring are known as benzylic halides.

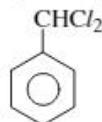
In alkyl halides, allyl halides and benzyl halides, halogen atom is bonded to an sp^3 hybridized carbon atom. In aryl halides and vinyl halides, halogen atom is bonded to an sp^2 hybridized carbon atom.



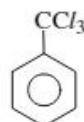
Benzylic halides : If halogen atom is attached to a benzylic carbon, i.e., the carbon atom of the side chain carrying the aryl group, they are benzylic halides.



Benzyl chloride

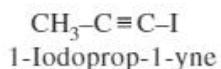
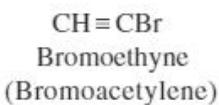


Benzal chloride



Benzo trichloride

Alkynyl halides : In these halides, the halogen atom is attached to one of the carbon atoms of a $\text{C}\equiv\text{C}$.



1.1.2

Nomenclature

The common names of alkyl halides are derived by naming the alkyl group followed by the halide. The IUPAC name of an alkyl halide is haloalkane. The common and IUPAC names of some halogen derivatives are mentioned in Table 1.1.



P.1.1 Give the IUPAC names of the compounds. Classify them as alkyl, allylic, benzylic, vinylic and aryl halides and also as primary, secondary and tertiary halides.

(i) $(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{Cl})\text{CH}_3$, (ii) $\text{CH}_3\text{CH}_2\text{CH=CHCH}_2\text{Cl}$, (iii) $(\text{CH}_3)_2\text{CHCH}_2\text{CH=C(Cl)CH}_2\text{CH}_3$ and (iv) $\text{C}_6\text{H}_5\text{C}(\text{Cl})(\text{CH}_3)_2$

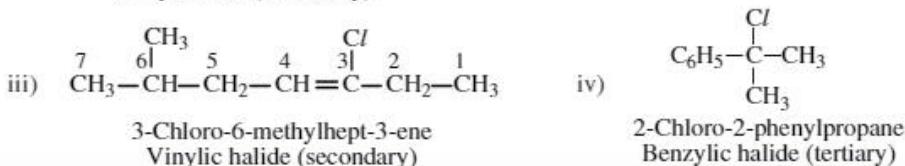
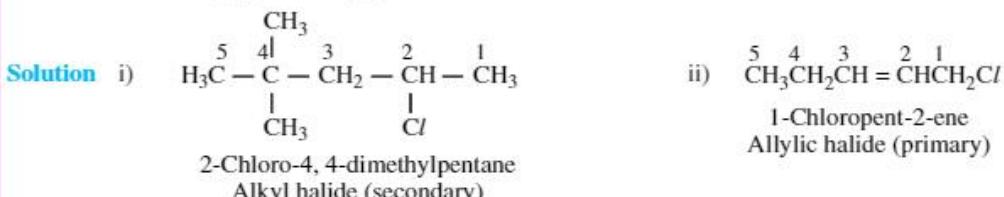
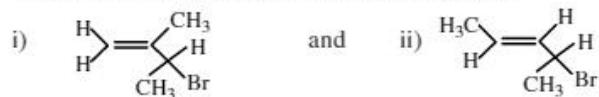


Table 1.1 Common and IUPAC names of some halogen derivatives

S.No.	Structure	Common name	IUPAC name
1	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	n-Butyl chloride	1-Chlorobutane
2	$(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$	iso-Butyl chloride	1-Chloro-2-methylpropane
3	$\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2\text{CH}_3$	sec-Butyl chloride	2-Chlorobutane
4	$(\text{CH}_3)_3\text{CBr}$	tert-Butyl bromide	2-Bromo-2-methylpropane
5	$(\text{CH}_3)_3\text{CCH}_2\text{Br}$	neo-Pentyl bromide	1-Bromo-2,2-dimethylpropane
6	$\text{CH}_2=\text{CHCH}_2\text{Cl}$	Allyl chloride	3-Chloropropene
7	$\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$	Ethylene chloride	1,2-Dichloroethane
8	$\text{CH}_3-\text{CHCl}_2$	Ethyldene chloride	1,1-Dichloroethane
9	CHCl_3	Chloroform	Trichloromethane
10	CCl_4	Carbontetrachloride	Tetrachloromethane
11	$\text{CH}_3\text{CH}_2\text{CH}_2\text{F}$	n-Propyl fluoride	1-Fluoropropane
12	$\text{CF}_3\text{CHC/Br}$	Halothane	2-Bromo-2-chloro-1,1,1-trifluoroethane
13		ortho-Chlorotoluene	1-Chloro-2-methylbenzene
14		Benzyl chloride	Chlorophenylmethane



P.1.2 Write IUPAC names of the following compounds :

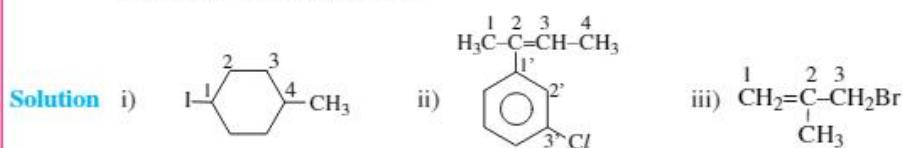


Solution The IUPAC names are : i) 3-Bromo-2-methylbut-1-ene and ii) 4-Bromopent-2-ene.



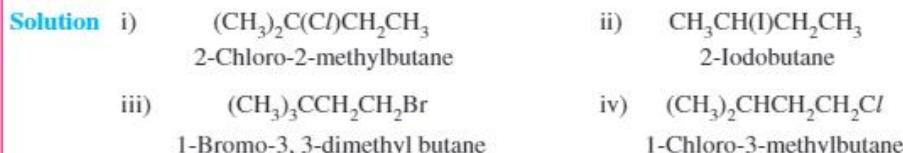
P.1.3 Write the structures of the following compounds :

- (i) 1-Iodo-4-methylcyclohexane
- (ii) 2-(3'-Chlorophenyl)but-2-ene
- (iii) 3-Bromomethylpropene



P.1.4 Give structural formulae and IUPAC names of the following compounds :

- (i) tert-Amyl chloride ; (ii) sec-Butyl iodide ; (iii) neo-Hexyl bromide and (iv) iso-Pentyl chloride.





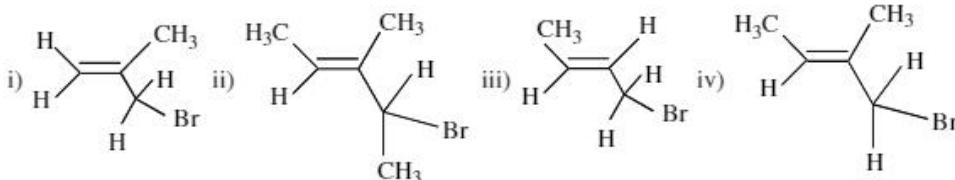
P.1.5 With molecular formula, $C_5H_{11}Br$; there are eight structural isomers. Give the IUPAC name of each isomer and classify them as primary, secondary or tertiary bromides.

Solution

$CH_3CH_2CH_2CH_2CH_2Br$	1- Bromopentane (1°)
$CH_3CH_2CH_2CH(Br)CH_3$	2-Bromopentane (2°)
$CH_3CH_2CH(Br)CH_2CH_3$	3-Bromopentane (2°)
$(CH_3)_2CHCH_2CH_2Br$	1- Bromo-3-methylbutane (1°)
$(CH_3)_2CHCH(Br)CH_3$	2- Bromo-3-methylbutane (2°)
$(CH_3)_2CBrCH_2CH_3$	2- Bromo-2-methylbutane (3°)
$CH_3CH_2CH(CH_3)CH_2Br$	1- Bromo-2-methylbutane (1°)
$(CH_3)_3CCH_2Br$	1- Bromo-2,2-dimethylpropane (1°)



P.1.6 Write IUPAC names of the following :

**Solution**

- | | |
|----------------------------|--------------------------------|
| i) 3-Bromo-2-methylpropene | ii) 4-Bromo-3-methylpent-2-ene |
| iii) 1-Bromobut-2-ene | iv) 1-Bromo-2-methylbut-2-ene |

1.1.3**Isomerism**


Alkyl halides with four or more carbon atoms with asymmetric carbon centre exhibit optical isomerism


Higher members of alkyl halides show mainly three types of isomerism.

Chain isomerism

The haloalkanes with four or more carbon atoms exhibit chain isomerism. This is due to different arrangement of carbon atoms in the alkyl group.

**Position isomerism**

The haloalkanes with three or more carbon atoms show positional isomerism.

**Optical isomerism**

The haloalkanes with four or more carbon atoms with asymmetric carbon atom exhibit optical isomerism. eg : 2-Bromobutane.

The total number of isomers in alkyl halides : Propyl halide (C_3H_7-X) has two isomers, butyl (C_4H_9-X) has five isomers and pentyl ($C_5H_{11}-X$) has eleven isomers.

Conformations : Alkyl halides can also form conformers due to the free rotation of C–C bond.



P.1.7 A saturated hydrocarbon, C_6H_{14} gives two monochloro compounds on chlorination. Identify the hydrocarbon.

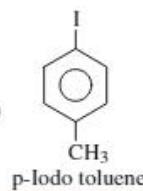
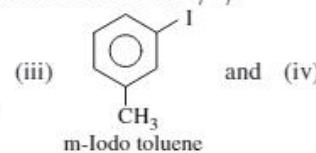
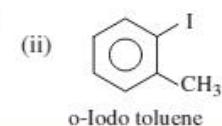
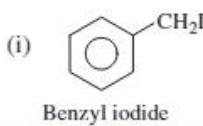
Solution

Since the hydrocarbon gives two monochloro derivatives, it indicates that it contains two equivalent hydrogens. The hydrocarbon is 2,3-dimethylbutane.



P.1.8 Write the structures of all aromatic iodides with the formula C_7H_7I .

Solution There are four structural aromatic iodides with the formula, C_7H_7I .



1.1.4

Nature of C-X bond

With increase in size of X, bond length increases but bond enthalpy decreases

The carbon atoms in alkyl halides are all sp^3 hybridised and are approximately tetrahedral (bond angles are around 109°). The C–H and C–C bonds are formed by the sp^3 – 1s and sp^3 – sp^3 linear overlap respectively.

Due to more electronegativity of halogen than carbon, halogen atom of carbon-halogen bond bears a partial negative charge and carbon, a partial positive charge.



With increase in size of the halogen atom, bond length gradually increases and enthalpy gradually decreases. Some typical bond lengths, bond enthalpies and dipole moments are given in Table 1.2.

Table 1.2 Carbon-halogen (C–X) bond lengths, bond enthalpies and dipole moment of some molecules

Methyl halide	C–X Bond length (Å)	Bond enthalpy (kJ mol ⁻¹)	Dipole moment (Debye)
H_3C-F	1.39	452	1.847
H_3C-Cl	1.78	351	1.860
H_3C-Br	1.93	293	1.830
H_3C-I	2.14	234	1.636

EXERCISE - 1.1.1

- What are geminal halides and vicinal halides? Give examples.
- Give one example each for aryl halide and aryl alkyl halide.
- Give IUPAC names of isobutyl chloride, neohexylchloride and tertiary butylchloride.
- What type of isomerism can be exhibited by alkyl halides having three or more carbon atoms?
- Give the names and structures of different isomers with formula C_4H_9Cl .
- Discuss the polarity of carbon-halogen bond in alkyl halides.

ETHYL CHLORIDE

1.2.1

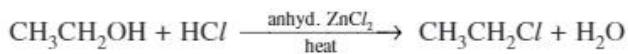
Preparation From alcohols

By reaction with halogen acids : The hydroxyl group of an alcohol is replaced by halogen on reaction with concentrated halogen acids. Alcohols are converted to alkyl halides. This is nucleophilic substitution.



Lucas reagent is a mixture of anhydrous $ZnCl_2$ and conc. HCl

The reaction is carried out in presence of anhydrous $ZnCl_2$ which acts as catalyst for dehydration. The mixture of concentrated HCl and anhydrous $ZnCl_2$ is called Lucas reagent.

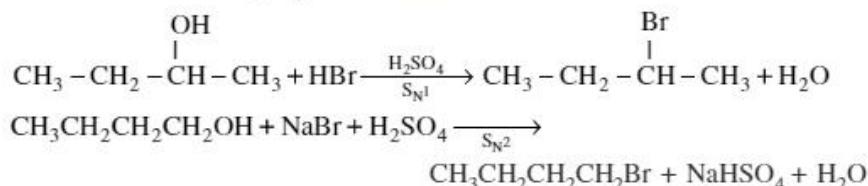


The process of using HCl gas and anhydrous $ZnCl_2$ is called as Groove's process. Pyridine, dimethyl amine and concentrated sulphuric acid are also used as catalyst for this reaction. Tertiary alcohols readily react with concentrated HCl even in the absence of $ZnCl_2$.

Bromoalkanes can be obtained by heating alcohols with KBr or $NaBr$ and concentrated H_2SO_4 .



The alcohols react with HBr generated by the reaction of $NaBr$ or KBr with H_2SO_4 . Secondary alcohols react with HBr by way of S_N1 mechanism, but the primary alcohols react with HBr by S_N2 mechanism.

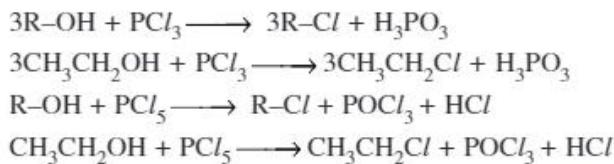


Iodoalkanes can be prepared by refluxing alcohol with 57% hydriodic acid or potassium iodide in presence of phosphoric acid.

Reactivity of halogen acids towards this reaction is : $HI > HBr > HCl$.

Reactivity of alcohols towards this reaction is : Benzylic > allylic > tertiary > secondary > primary.

By reaction with phosphorus halides : Chloroalkanes are obtained by reaction of alcohols with phosphorus pentachloride or phosphorus trichloride.

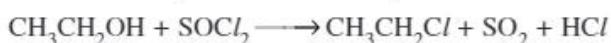


Bromo and iodo alkanes are obtained by reaction of alcohols with a mixture of red phosphorus and bromine or iodine. The function of red phosphorus and bromine or iodine is to get PBr_3 and PI_3 during the course of the reaction which are relatively unstable and have to be prepared *in situ*.

The method gives good yield of primary alkyl halides but poor yields of secondary and tertiary alkyl halides. Tertiary alcohols mainly undergo elimination reactions. This method is mainly useful for preparing lower alkyl bromides and iodides in the laboratory.

By reaction with thionyl chloride : When the alcohol is refluxed with thionyl chloride in the presence of a small amount of pyridine, alkyl chloride is formed in pure form. Pyridine neutralises both the byproducts in the reaction. Hence thionyl chloride is preferred. This method is called Darzen's method.

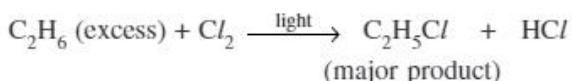
Thionyl chloride is a better reagent for preparing alkyl halide from alcohol



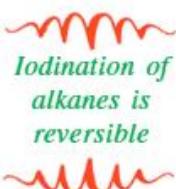
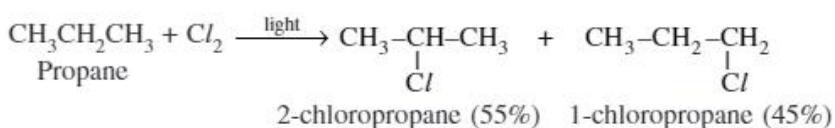
From alkanes

When alkanes are treated with chlorine or bromine in the presence of sun light or heat, a mixture of mono and poly substituted products is formed. Although, the halogenation beyond monohalogenation may be suppressed by using alkane in excess, yet the method is not of much practical use. This is because of the difficulties of separation of such a mixture. Chlorination of alkanes is free radical substitution. The reactivity of the various types of C-H bonds is in the following order :

Allylic = benzylic > tertiary > secondary > primary.



In case of higher alkanes, different isomeric products are formed even when monosubstitution is carried out.

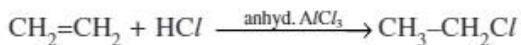


The iodination of alkanes is reversible and is carried out by heating with iodine in the presence of oxidising agents like concentrated HNO_3 , HIO_4 or HIO_3 . Fluorination takes place explosively. Therefore, alkyl fluorides are prepared by indirect method.

From alkenes

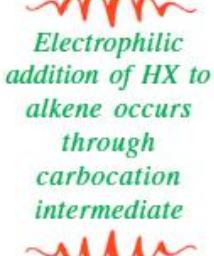
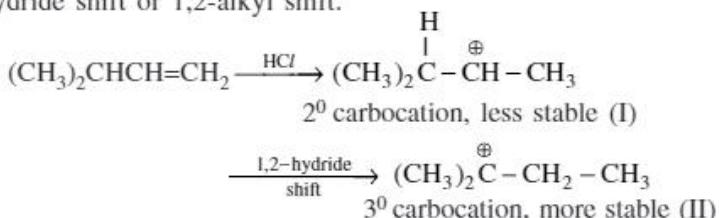
Halogen acids (HCl , HBr , HI) react readily with alkenes to form alkyl halides. This reaction involves electrophilic addition.

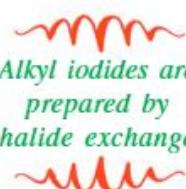
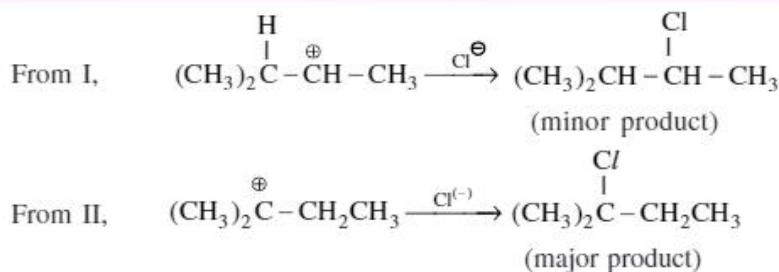
The order of reactivity is : $\text{HI} > \text{HBr} > \text{HCl}$.



In unsymmetrical alkenes, the addition of halogen acids takes place according to Markovnikov's rule. Addition of HBr to unsymmetrical alkenes in the presence of peroxide takes place according to anti Markovnikov's rule via free radical addition mechanism.

Electrophilic addition of hydrogen halides to alkenes occurs through carbocation intermediates. Hence this reaction involves rearrangement to more stable carbocation by 1,2-hydride shift or 1,2-alkyl shift.





Alkyl iodides are prepared by halide exchange

Halide exchange

This is a convenient method for the preparation of alkyl iodides. The corresponding alkyl bromides or chlorides are treated with a solution of sodium iodide in acetone.



This reaction is known as **Finkelstein reaction**. This reaction is based on the fact that sodium iodide is soluble in acetone but sodium bromide and sodium chloride are insoluble. It facilitates the forward reaction according to Le Chatelier's principle.

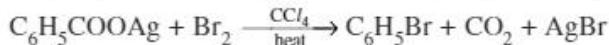
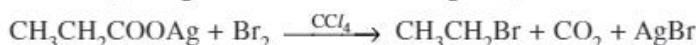
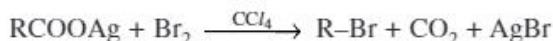
The synthesis of alkyl fluoride is best accomplished by heating an alkyl chloride or bromide in the presence of a metallic fluoride such as AgF , Hg_2F_2 , CoF_2 or SbF_3 . This reaction is known as **Swarts reaction**.



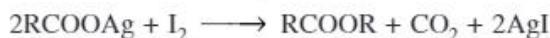
Silver acetate on refluxing with bromine in tetrachloromethane gives ethylbromide

From silver salts of fatty acids

Bromoalkanes are obtained by refluxing silver salts of fatty acids with bromine in carbon tetrachloride. (Decarboxylative bromination).

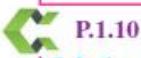
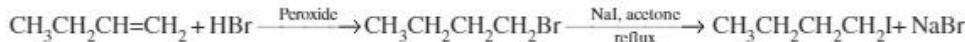


The reaction is known as **Borodine-Hunsdiecker reaction** and can be employed for descending of series. This reaction gives the product with one carbon atom less than the fatty acid. Chloroalkanes can also be obtained by this reaction, however, the yield is low. Iodoalkanes, however cannot be obtained by this reaction. Iodine forms ester instead of alkyl halide and is called **Birnbaum-Simonini reaction**.



P.1.9 How is 1-iodobutane obtained from 1-butene

Solution Through Kharasch effect and halide exchange, 1-iodobutane is obtained.

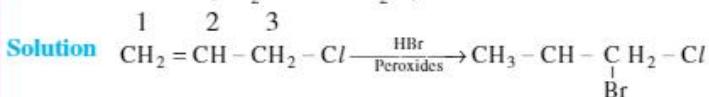


P.1.10 What is the major product obtained by mono-chlorination of 2-methylbutane.

Solution 2-methylbutane give form mono chlorination products. Among the form 2-chloro 3-methyl is the major product, following the reactivity, selectivity.



P.1.11 Give the structures of the product obtained by addition HBr in presence of peroxide to allyl chloride ($\text{CH}_2 = \text{CH} - \text{CH}_2\text{Cl}$)



Due to the inductive effect of chlorine, the initial radical formed on the first carbon atom more stable and hence the product.

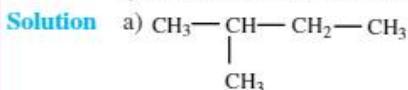


P.1.12 During the reaction of alcohols with KI, why sulphuric acid is not used?

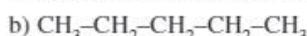
Solution In the conversion of alcohol to alkyl iodide, H_2SO_4 cannot be used since it converts KI to corresponding HI and then oxidises it to iodine.



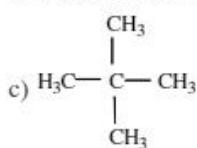
P.1.13 Among the three isomeric alkanes (C_5H_{12}), identify the one that on chlorination yields
a) Four isomeric monochlorides; b) Three isomeric monochlorides ; c) A single monochloride



In methylbutane, there are four different carbon atoms and hence four different hydrogen atoms. Thus, four isomeric products are possible.



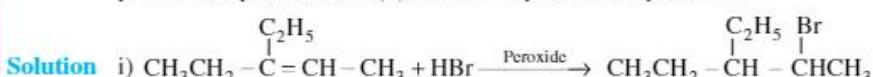
In pentane, there are three different carbon atoms and hence three different hydrogen atoms. Then, three isomeric products are possible.



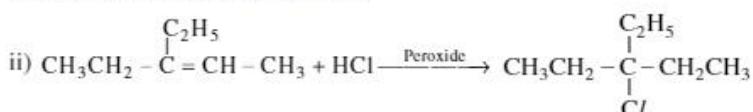
In dimethylpropane, all the hydrogen atoms are equivalent. Hence only one isomeric product is possible.



P.1.14 Give the structures of the major organic products from 3-ethyl-2-pentene using (i) HBr in the presence of peroxide and (ii) HCl in the presence of peroxide.



This is anti-Markovnikoff addition



This is Markovnikoff addition, since peroxide effect is not observed in HCl.

1.2.2

Physical properties Alkyl halides are colourless when pure. However, bromides and iodides develop colour when exposed to light. Many volatile halogen compounds have sweet smell. CH_3F , CH_3Cl , CH_3Br and $\text{C}_2\text{H}_5\text{Cl}$ are gases at room temperature. The alkyl halides upto C_{18} are colourless liquids while higher members are colourless solids.

Alkyl halides are insoluble in water because they are not able to form hydrogen bonds with water molecules. However, they are soluble in organic solvents such as alcohol, ether, benzene, etc.

Alkyl bromides and iodides are generally heavier than water. Alkyl fluorides and alkyl chlorides are lighter than water. The densities of alkyl halides are in the order : R-I > R-Br > R-Cl. In general, the density of halogen derivatives increases with increase in number and atomic mass of the halogen atoms. The density of poly halogen derivatives of methane is in the order : $\text{CCl}_4 > \text{CHCl}_3 > \text{CH}_2\text{Cl}_2$.

For the same alkyl group, the boiling points of alkyl halides decrease in the order : R-I > R-Br > R-Cl > R-F. This is because with the increase in size and mass of halogen atoms, the magnitude of van der Waals forces increases.

Alkyl halide	CH_3I	CH_3Br	CH_3Cl	CH_3F
Boiling point	316K	278K	249K	195K

Among isomeric alkyl halides, boiling point decreases with increase in branching

The boiling points of various halogen compounds increase with increase in number of halogen atoms. Among isomeric alkyl halides, the boiling point decreases with increase in branching in the alkyl group. This is due to the reason that with increase in branching, the molecule attains spherical shape with less surface area.

Alkyl Halide	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ (1°)	$\text{CH}_3\text{CH}_2\overset{\text{CH}_3}{\underset{\text{Br}}{ }\text{CHCH}_3}$ (2°)	$\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{Br}}{ }\text{C}-\text{CH}_3}$ (3°)
Boiling point	375 K	364 K	346 K

Boiling points of isomeric dihalobenzenes are very nearly the same. However, the melting points of para-isomers are high due to symmetry of isomers that fits in crystal lattice better compared to meta- and ortho- isomers.

Dihalobenzene	Melting point	Boiling point
ortho-dichlorobenzene	256 K	453 K
meta-dichlorobenzene	249 K	444 K
para-dichlorobenzene	323 K	448 K

Solubility of haloalkanes in water is less. They dissolve in organic solvents, as the attractions between haloalkane and solvent molecules are predominant compared to attractions between molecules of haloalkane and molecules of solvent.



P.1.15 Which isomer of $\text{C}_5\text{H}_{11}\text{Cl}$ has the highest boiling point and which has the least boiling point ? Explain.

Solution 1-Chloropentane has the highest boiling point whereas 1-chloro-2,2-dimethylpropane has the least boiling point. 1-Chloropentane is the unbranched chain isomer with strongest interparticle forces. 1-Chloro-2,2-dimethyl propane has weakest inter particle forces due to smallest surface area with spherical symmetry.

1.2.3

Chemical properties Haloalkanes are highly reactive class of aliphatic compounds. Their reactivity is due to the presence of polar carbon-halogen bond in their molecules.

Larger the bond dissociation energy of C-X bond, smaller is the reactivity. The bond dissociation energy order is : C-Cl > C-Br > C-I. For a given alkyl group, the order of reactivity is : iodide > bromide > chloride.

Characteristic reactions of alkyl halides are nucleophilic substitution reactions

The rate of S_N^2 reaction depends upon concentration of alkyl halide and nucleophile

The reactions of halo alkanes may be divided into four types:

Nucleophilic substitution reactions, elimination reactions, reaction with metals, reduction reactions and Friedel-Craft's reactions.

I. Nucleophilic substitution reactions

In haloalkanes, the bond between carbon and halogen is polar and hence carbon atom gets partial positive charge and halogen atom gets partial negative charge. A nucleophile reacts with haloalkane having a partial positive charge on the carbon atom bonded to halogen. A substitution reaction takes place and halogen atom, called leaving group departs as halide ion. Since the substitution reaction is initiated by a nucleophile, it is called nucleophilic substitution reaction. Thus, typical reactions of alkyl halides are nucleophilic substitution reactions.



Halide ions are substituted when the attacking nucleophile is stronger than it. C-F bond is so strong that organic fluorides do not undergo nucleophilic substitution under ordinary conditions. The products of haloalkanes with some nucleophiles are given in Table 1.3.

Nucleophilic substitution reactions in halides containing $\text{sp}^3\text{C}-\text{X}$ bond may take place either of the two different mechanisms.

Second order nucleophilic substitution : This is also called bimolecular nucleophilic substitution or substitution nucleophilic bimolecular. The rate of this reaction is dependent on the concentration of alkyl halide as well as nucleophile.

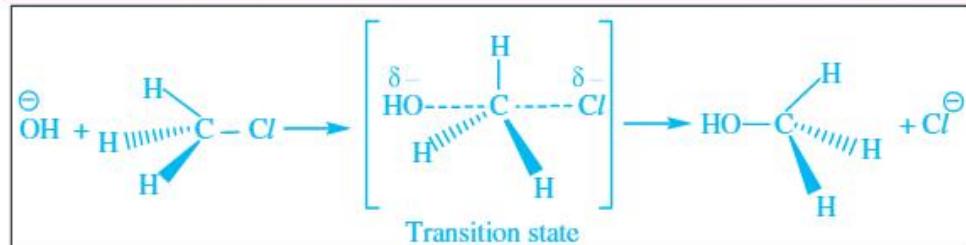
$$\text{Rate} = k[\text{RX}] [\text{Nu}^-]$$

Primary alkyl halides react by S_N^2 mechanism via formation of a transition state. The reaction between methyl chloride and hydroxide ion to yield methanol and chloride ion follows a second order kinetics.

Table 1.3 Products of haloalkanes with some nucleophiles

Nucleophile product R-Nu	Reagent (Nu^-)	Substitution product	Class of main
NaOH (KOH)	HO^-	ROH	Alcohol
H_2O	H_2O	ROH	Alcohol
NaOR'	$\text{R}'\text{O}^-$	ROR'	Ether
NaI	I^-	R-I	Alkyl iodide
NH_3	NH_3	RNH_2	Primary amine
$\text{R}'\text{NH}_3$	$\text{R}'\text{NH}_2$	RNHR'	Sec. amine
$\text{R}'\text{R}''\text{NH}$	$\text{R}'\text{R}''\text{NH}$	$\text{RNR}'\text{R}''$	Tert. amine
KCN	$\bar{\text{C}} \equiv \text{N}:$	RCN (cyanide)	Nitrile
AgCN	$\text{Ag}-\text{NC}:^-$	RNC (isocyanide)	Isonitrile
KNO_2	$\text{O}=\text{N}-\text{O}^-$	$\text{R}-\text{O}-\text{N}=\text{O}$	Alkyl nitrile
AgNO_2	$\text{Ag}-\ddot{\text{O}}-\text{N}=\text{O}$	$\text{R}-\text{NO}_2$	Nitroalkane
$\text{R}'\text{COOAg}$	$\text{R}'\text{COO}^-$	$\text{R}'\text{COOR}$	Ester
LiAlH_4	H	RH	Hydrocarbon
$\text{R}'-\text{M}^+$	R'^-	RR'	Alkane


Formation of transition state is observed in S_N^2 mechanism

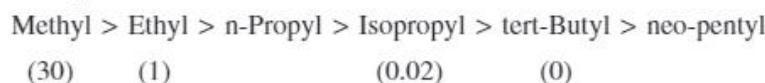
Hydroxide ion is a strong nucleophile (donor of an electron pair) because the oxygen atom has unshared pairs of electrons and a negative charge. Chloromethane is called the substrate, meaning the compound that is attacked by the reagent. The carbon atom of chloromethane is electrophilic because it is bonded to an electronegative chlorine atom. Electron density is drawn away from carbon by the halogen atom, giving the carbon atom a partial positive charge. Hydroxide ion attacks the back side of the electrophilic carbon atom, donating a pair of electrons to form a new bond. Carbon can accommodate only eight electrons in its valence shell, so the carbon-chlorine bond must begin to break as the carbon-oxygen bond begins to form.

Chloride ion is the leaving group ; it leaves with the pair of electrons that once bonded it to the carbon atom. The reaction of methyl chloride with hydroxide ion is a concerted reaction, taking place in a single step with bonds breaking and forming at the same time. The middle structure is a transition state, a point of maximum energy, rather than an intermediate. In the transition state, the bond to the nucleophile (hydroxide) is partially formed, and the bond to the leaving group (chloride) is partially broken. This transition state is not a discrete molecule and cannot be isolated. The rate is found to double when the concentration of either reactant is doubled. The reaction is therefore first order in each of the reactants and second order overall.


Leaving group is pushed away by the incoming nucleophile, causing Walden's inversion


As the reaction progresses, the configuration of carbon atom under attack inverts in the same way as an umbrella is turned inside out when caught in a strong wind. The leaving group is pushed away by the incoming nucleophile. This process is called as Walden's inversion of configuration.

Since the reaction requires the approach of the nucleophile to the carbon bearing the leaving group, the presence of bulky substituents on or near the carbon atom have a dramatic inhibiting effect. The order of reactivity of various alkyl halides through S_N^2 mechanism is:



The relative rates of S_N^2 reaction is given in parenthesis.

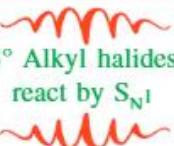
Thus the order of reactivity of various alkyl halides through S_N^2 mechanism for the given halide is: Methyl > Primary > Secondary > Tertiary.

Better will be the leaving group, faster will be the rate.



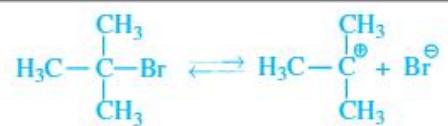
First order nucleophilic substitution : This is also called unimolecular nucleophilic substitution or substitution nucleophilic unimolecular. The rate of this reaction is dependent on the concentration of only one reactant, alkyl halide.

$$\text{Rate} = k[\text{RX}]$$

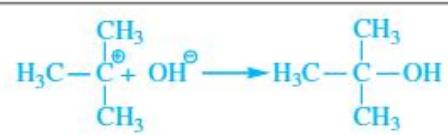

 3° Alkyl halides react by S_N1

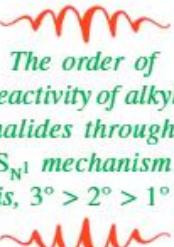
The tertiary alkyl halides react by S_N1 mechanism via formation of carbocation as intermediate. The reaction between tert-butyl bromide and hydroxide ion yields tert-butyl alcohol and follows first order kinetics. It occurs in two steps:

Step - I : In the first step, the alkyl halide slowly dissociates into halide ion and carbocation.



Step - II : In the second step, carbocation at once combines with the nucleophile to form the final substituted product.




It is interesting to note that its rate does not depend upon the concentration of hydroxide ion, the nucleophile. The rate depends only on the concentration of the substrate, tert-butyl bromide. This reaction follows overall first order. It is first order with respect to the alkyl halide and zeroth order with respect to the nucleophile. Step - I is the slowest and reversible. It involves the C-Br bond breaking for which the energy is obtained through solvation of halide ion with the proton of protic solvent. Therefore S_N1 reactions are generally carried out in polar protic solvents like water, alcohol, acetic acid, etc. Greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction.

Thus, the order of reactivity of various alkyl halides through S_N1 mechanism is:
Tertiary > Secondary > Primary > Methyl.

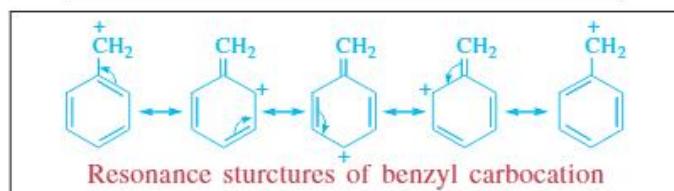
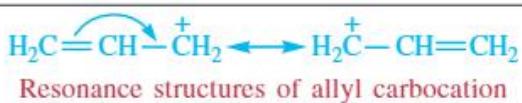
The order of reactivity of alkyl halides towards S_N1 and S_N2 reactions can be summed up as follows:

For S_N2 reaction

Tertiary halide	Secondary halide	Primary halide	Methyl halide
For S_N1 reaction			

For a given alkyl group, the reactivity of the halide, R-X, follows the same order in both the mechanisms : R-I > R-Br > R-Cl > R-F.

Primary allylic and benzylic halides show greater reactivity through S_N1 mechanism than tertiary alkyl halides. This is due to greater stability of allylic and benzylic carbocations than tertiary alkyl carbocations due to resonance stabilisation.




**Allylic and
benzylic
carbocations are
more stable than
primary alkyl
carbocations due
to resonance**



**Tertiary halides
undergo substitution
exclusively
through S_N1
mechanism**



**Good ionising
solvent favours
 S_N1 and less
polar solvent
favours S_N2**


Starting with an optically active alkyl halide, the reaction through S_N1 mechanism results in partial racemisation. Because of the planarity of the carbocation, the nucleophile can attack from either side resulting in the formation of both enantiomers. The two enantiomers are not formed in exactly equal amounts resulting in partial racemisation since the attack from back side is slightly more probable.

Vinyl and aryl halides are unreactive towards both S_N1 and S_N2 .

Comparision of S_N1 and S_N2 reactions

Effect of the nucleophile : A strong nucleophile promotes the S_N2 mechanism. Weak nucleophiles fail to promote the S_N2 reaction; therefore, often go by the S_N1 mechanism if the substrate is secondary or tertiary.

S_N1 : Nucleophile strength is unimportant.

S_N2 : Strong nucleophiles are required.

In S_N2 reaction of CH_3I nucleophilicity order of various nucleophiles :



Effect of the substrate : Methyl halides and primary halides cannot easily ionise and undergo S_N2 substitution because methyl and primary carbocations are high in energy. They are relatively unhindered, however they make good S_N2 substrates. Tertiary halides are hindered to undergo S_N2 displacement, but they can ionise to form tertiary carbocations. Tertiary halides undergo substitution exclusively through the S_N1 mechanism. Secondary halides can undergo substitution by either mechanism, depending on the conditions.

S_N1 substrates : $3^0 > 2^0$; (1^0 and CH_3X are unlikely).

S_N2 substrates : $\text{CH}_3\text{X} > 1^0 > 2^0$; (3^0 is not suitable).

Effect of solvents : Very polar ionising solvents such as water and alcohols are needed for the S_N1 . S_N2 reaction often goes faster in less polar solvents. However, polar aprotic solvents may enhance the reactivity with weak nucleophiles.

S_N1 : Good ionising solvent required.

S_N2 : May go faster in a less polar solvent.

Kinetics : The rate of the S_N1 reaction is proportional to the concentration of the alkyl halide but not the concentration of the nucleophile. It follows a first order reaction kinetics. The rate of the S_N2 reaction is proportional to the concentrations of both the alkyl halide and the nucleophile. It follows a second order rate equation.

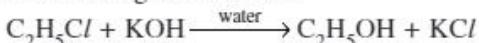
Stereochemistry : The S_N1 reaction involves a flat carbocation intermediate that can be attacked from either face. Therefore, the S_N1 usually gives a mixture of products with inversion and retention of configuration. The S_N2 reaction takes place through a back-side attack, which inverts the stereochemistry of the carbon atom. Complete inversion of configuration takes place.

S_N1 stereochemistry : Mixture of products with retention, inversion and racemisation. S_N2 stereochemistry : Complete inversion.

Rearrangements : The intermediate carbocation can rearrange, usually a hydride shift or an alkyl shift takes place to give a more stable carbocation. The S_N2 reaction takes place in one step with no intermediates. No rearrangement is possible in the S_N2 reaction.

Rearrangements are likely to occur in S_N1 and not likely in S_N2 .

Replacement by hydroxyl group : Haloalkanes on treating with boiling aqueous alkali solution give alcohols.



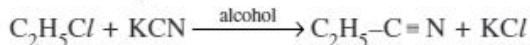
Alkyl halides give cyanides as main products with KCN

Alkyl halides give isocyanides as main products with AgCN

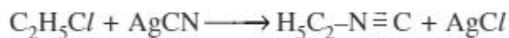
Haloalkanes are hydrolysed to corresponding alcohols by moist silver oxide.



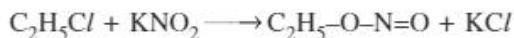
Replacement by cyano group : Haloalkanes on treatment with alcoholic potassium cyanide solution give alkane nitriles as the major product with a small amount of isocyanide.



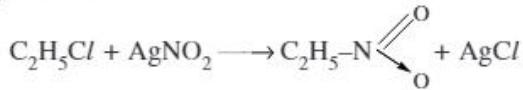
Replacement by isocyanide group : Alkyl halides react with aqueous ethanolic silver cyanide to form alkyl isocyanide as major product with a small amount of alkyl cyanide.



Replacement by nitrite group : Alkyl halides react with potassium or sodium nitrite to give alkyl nitrites as the major product. With dimethyl formamide as solvent, about 30% of alkyl nitrite is formed.



Replacement by nitro group : On treating ethanolic solution of haloalkanes with silver nitrite, the major product formed is nitro alkane and the minor product is alkyl nitrite.



However, the percentage of the product of the reaction between alkyl halide and potassium or silver nitrite depends upon the solvent used.

Nucleophiles such as cyanide and nitrite ion which can attack nucleophilic centre from two sides are called ambident nucleophiles. Actually cyanide group is a hybrid of two contributing structures and therefore can act as a nucleophile in two different ways. Linkage through carbon atom results an alkyl cyanide and through nitrogen atom results an isocyanide. Similarly nitrite ion represents as a resonance hybrid. The linkage through nitrogen results nitroalkane and through oxygen results alkyl nitrite.

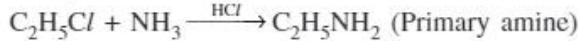
Replacement by alkoxy group : Ethers are formed when haloalkanes are treated with alcoholic sodium or potassium alkoxide. This reaction is known as **Williamson synthesis**.



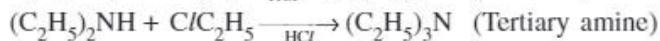
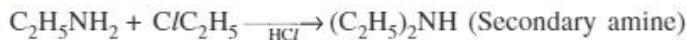
Ether can also be obtained from alkyl halide using dry silver oxide.



Replacement by amino group : On heating with aqueous or alcoholic solution of ammonia in a sealed tube at 100°C, alkyl halides yield a mixture of amines and quaternary ammonium salt.



In case, haloalkane is in excess, the other two hydrogen atoms of amino group are replaced by alkyl groups leading to the formation of secondary and tertiary amines.



Final product of Hofmann ammonolysis of alkyl halides is quaternary ammonium salt

Tertiary amine so formed can further combine with another molecule to give quaternary ammonium salt as the product.



This reaction is known as **Hofmann ammonolysis** of alkyl halides.

Replacement by hydrosulphide group : Potassium or sodium hydrogen sulphide reacts with haloalkanes to give thioalcohols.



Replacement by alkynyl group : Alkyl halides react with sodium acetylide to form higher alkynes.



Reaction with halides : Alkyl chlorides react with sodium or potassium bromide or iodide to form alkyl bromide or alkyl iodide.



Replacement by carboxylate : Alkyl halides react with silver acetate in alcoholic solution to form esters.



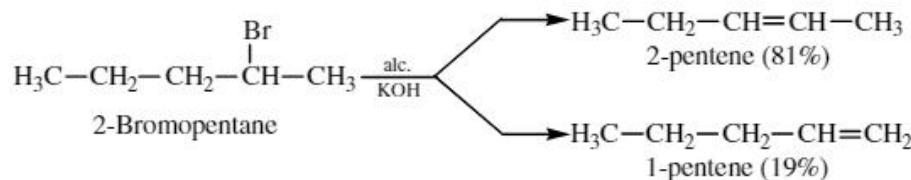
II. Elimination reactions

When haloalkanes are heated with alcoholic potassium hydroxide, they undergo dehydrohalogenation to form alkenes. These reactions are called β -eliminations because the hydrogen atom present at β -position of the haloalkane is removed. Among various halides with same alkyl group, the order of reactivity is: R-I > R-Br > R-Cl.

This can be explained on the basis of the stability of the alkene formed after dehydrohalogenation. Tertiary alkyl halides on dehydrohalogenation form most substituted alkenes, which being more stable are formed at faster rate.

If there is possibility of formation of more than one alkene due to the availability of β -hydrogen atoms, usually one alkene is formed as the major product. This generalisation is known as **Saytzeff (Zaitsev) rule**, which can be summarised as, in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.

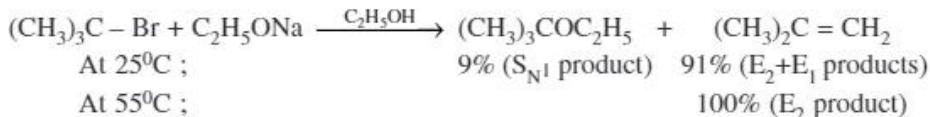
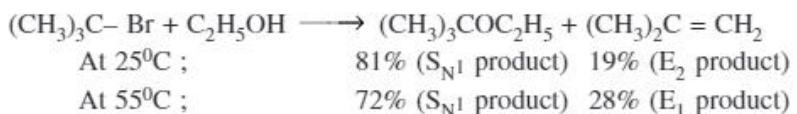
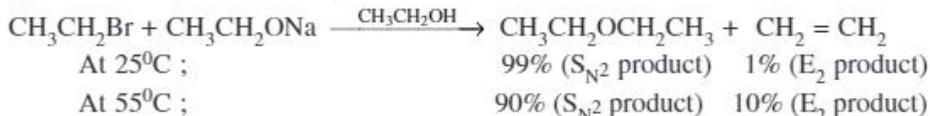
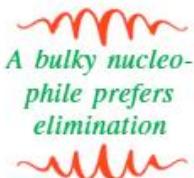
2-Bromopentane on dehydrohalogenation gives pent-2-ene as major product.



Substitution vs elimination : All nucleophiles are bases and all bases are nucleophiles. Therefore nucleophilic substitution and elimination reactions often compete with each other. Which reaction will be taken up depends upon the nature of alkyl halide, strength and size of nucleophile and reaction conditions.

The dehydrohalogenation can occur by either E₁ (unimolecular elimination) or E₂ (bimolecular elimination) mechanism depending on the structure and experimental conditions. The primary alkyl halides usually undergo S_N² and E₂ reactions.

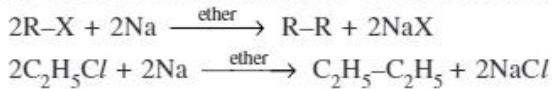
simultaneously, with the former predominating. The tertiary alkyl halides mainly form alkenes and very little substitution products, particularly when the base is strong and the temperature is high.



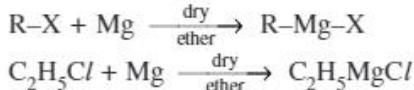
The most highly substituted alkene is the preferred product because it is formed faster than alternative alkenes. The ease of formation of alkenes is in the order $R_2C = CR_2 > R_2C = CHR > R_2C = CH_2 > RCH = CHR > RCH = CH_2 > CH_2 = CH_2$. The ease of dehydrohalogenation for given halogen is in the order : $3^0 > 2^0 > 1^0$.

III. Reaction with metals

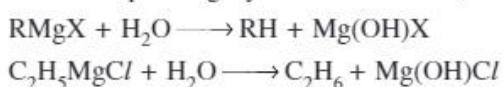
Reaction with sodium : Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the alkyl halide. This reaction is known as **Wurtz reaction**.



Reaction with magnesium : Alkyl halides form Grignard reagents when treated with magnesium powder in dry ether.

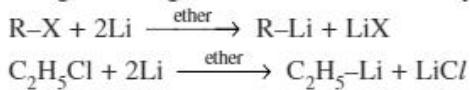


Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons. Even water, alcohol, amines are sufficiently acidic to convert them to corresponding hydrocarbons. Here, R^- acts as a strong base.

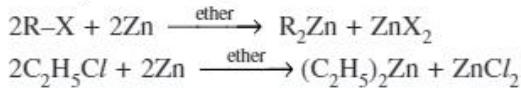


Reactivity order of Grignard reagents is: $\text{RMgI} > \text{RMgBr} > \text{RMgCl}$.

Reaction with lithium : Alkyl halides react with lithium in dry ether to form alkyl lithium which serves as a strong base. Alkyl lithiums are similar in properties with Grignard reagents. These are also very reactive reagents.

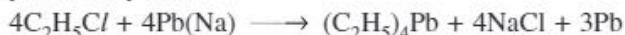


Reaction with Zinc : When heated with zinc powder in ether, alkyl halides form dialkyl zinc compounds called Frankland reagents.

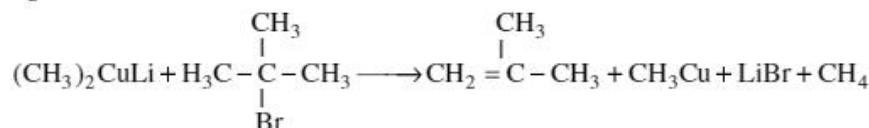
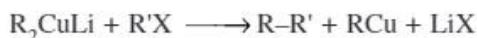
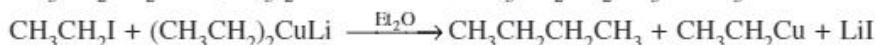
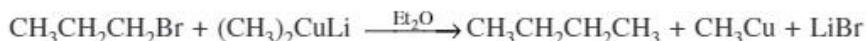



**Tetra ethyl lead
is prepared from
ethyl chloride
using
Pb-Na alloy**


Reaction with lead-sodium alloy : When heated with lead-sodium alloy in the presence of dry ether, ethyl chloride gives tetra ethyl lead which is used as antiknock compound in petrol.



Courey-House Synthesis of alkanes : Primary alkyl halides react with lithium dialkylcuprate (Gilman reagent) in anhydrous ether or THF to give alkanes in good yield. Secondary alkyl halides give poor yield of substitution product since elimination occurs to a considerable extent. Tertiary alkyl halides undergo solely elimination.



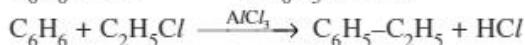
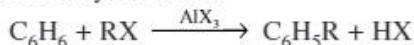
IV. Reduction

Alkanes are formed when alkyl halides are reduced with nascent hydrogen obtained by Zn and HCl or sodium and alcohol or lithium aluminium hydride or hydrogen in presence of nickel or palladium.



V. Friedel-Crafts reaction

Alkyl halides react with benzene in presence of anhydrous aluminium halides to form alkyl benzene.



Uses of ethyl chloride

Ethyl chloride is used as a refrigerant and a local anaesthetic. It is used in the preparation of tetraethyl lead (TEL) and also in the preparation of Grignard reagent which is very important in synthetic organic chemistry.



P.1.16 Why alkyl halides are not generally prepared in laboratory by free radical halogenation of alkanes?

Solution For the preparation of alkyl halides in the laboratory, free radical halogenation of alkanes is not a suitable method since it results in the formation of many isomeric monosubstituted products through substitution of different kinds of hydrogen atoms. Moreover, poly halogenation may also take place.



P.1.17 Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanide as the main product. Explain.

Solution KCN is mainly ionic compound and provides cyanide ions in solution. Though each carbon and nitrogen carry a lone pair of electrons, the lone pair on carbon is more reactive. The carbonium ion, R⁺, preferentially combines with the carbon atom of the cyanide group and forms alkyl cyanide.

On the other hand, AgCN is mainly a covalent compound and only nitrogen has the lone pair of electrons. Thus, carbonium ion attacks through nitrogen and thereby forms an alkyl isocyanide.



P.1.18 ROH cannot be converted into RC_l on treatment with KCl, however reaction takes place on treatment with HCl. Explain.

Solution Cl⁻ is a weak nucleophile than OH⁻ and hence cannot replace. However when HCl is added, H⁺ of HCl protonates on oxygen atom and H₂O becomes good leaving group and gives R-Cl



P.1.19 Optically active 2-iodobutane on treatment with sodium iodide in acetone gives a product which does not show optical activity. Explain.

Solution Optically active 2-iodobutane dissociated to form iodide ion and the carbocation. The iodide ion then attacks the flat carbocation from either side resulting in a mixture of two enantiomeric products in equal amounts, which constitutes a racemic mixture which does not show optical activity.



P.1.20 Predict the order of reactivity of the four isomeric bromobutanes in S_N¹ and S_N² reactions :

Solution CH₃CH₂CH₂CH₂Br < (CH₃)₂CHCH₂Br < CH₃CH₂CH(Br)CH₃ < (CH₃)₃CBr (S_N¹)
CH₃CH₂CH₂CH₂Br > (CH₃)₂CHCH₂Br > CH₃CH₂CH(Br)CH₃ > (CH₃)₃CBr (S_N²)



P.1.21 There are three outcomes of a substitution reaction at an asymmetric carbon of alkylhalide. Explain.

Solution If substitution is on the same side of leaving group retention of configuration occurs and on opposite side inversion of configuration occurs. If a 50:50 mixture of the two is obtained, the process is called racemisation.



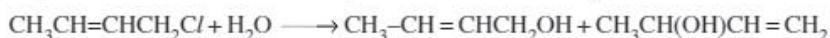
P.1.22 How do you distinguish between CH₃CH=CHCl; CH₃CH₂CH₂Cl and CH₂=CH-CH₂Cl?

Solution The Cl in CH₂=CHCH₂Cl is very reactive. This reacts rapidly with AgNO₃ in the cold to give a white precipitate of AgCl.

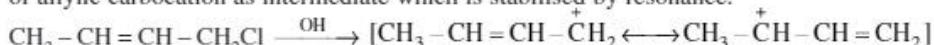
CH₃CH₂CH₂Cl gives white precipitate when warmed with AgNO₃ as it is comparatively less reactive. CH₃CH=CHCl is inert and does not form white precipitate with AgNO₃.



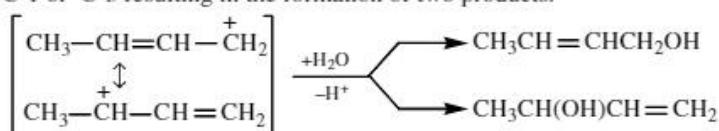
P.1.23 Explain the formation of the two products in the following reaction :



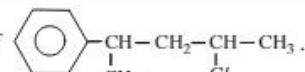
Solution Hydrolysis of 1-chloro-2-butene takes place through S_N¹ mechanism involving the formation of allylic carbocation as intermediate which is stabilised by resonance.



The positive charge is equally distributed over C-1 and C-3. The nucleophile can attack on C-1 or C-3 resulting in the formation of two products.



P.1.24 Predict the major product obtained by dehydrochlorination of



Solution The major product is

with benzene ring and hence the product is more stable.

P.1.25 Why the chlorine atom in vinyl chloride is non-reactive?

Solution The non-reactivity of chlorine atom in vinyl chloride is due to resonance stabilisation.

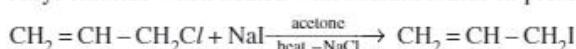


Carbon–chlorine bond in vinyl chloride has some double bond character and is, therefore, stronger than a pure single bond. Chlorine atom of vinyl chloride acquires positive charge, due to more dominant +M effect than –I effect.

1

P.1.26 Allyl iodide can be obtained from allyl chloride. Explain.

Solution Allyl chloride when heated with sodium iodide in presence of acetone, allyl iodide is formed.

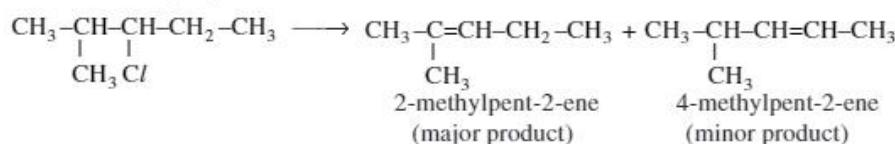


This is a halogen exchange reaction and is called Finkelstein reaction.

4

P.1.27 Write the structures of major and minor products formed when 3-chloro-2-methylpentane is subjected to dehydrohalogenation.

Solution The products of dehydrohalogenation are formed according to Saytzeff rule. More substituted alkene is the major product.



4

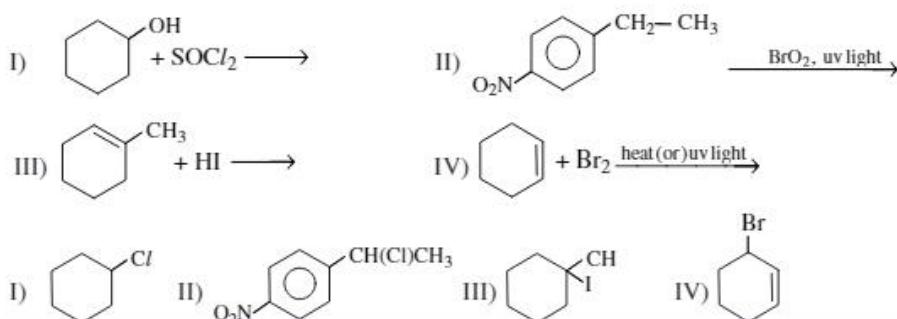
P1.28 Arrange each set of compounds in order of increasing boiling points.

- I) (a) Bromomethane ; (b) Bromoform ; (c) Chloromethane and (d) Dibromomethane
II) (p) 1-chloropropane : (q) Isopropyl chloride and (r) 1-Chlorobutane

Solution The increasing order of boiling points is I) $b > d > a > c$: II) $r > p > q$

4

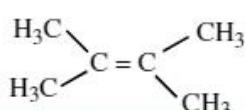
P1.29 Draw the structures of major products in each of the following reactions.



4

P1.30 2-Bromo-2,3-dimethylbutane is treated with alcoholic potash. Write the major product.

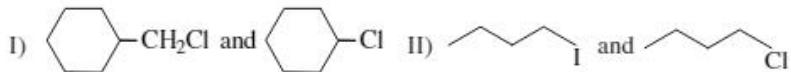
Solution Applying Zaitsev rule, bromine must be lost from C-2 and hydrogen from C-1 or C-3, during dehydrobromination reaction.



The major product is 2,3-dimethyl-2-butene.



P.1.31 In the following pairs of halogen compounds which would undergo S_N2 reaction faster?



Solution I) It is a primary halide and hence it is more reactive in S_N2

II) As I^- is good leaving group than Cl^- , is more reactive in S_N2 and S_N1 reactions.

EXERCISE - 1.1.2

- Explain the preparation of ethyl chloride from (i) ethyl alcohol, (ii) ethylene and (iii) ethane.
- Write two preparations and two important properties of ethyl chloride.
- How does ethyl chloride react with aqueous KOH and alcoholic KOH? Give equations.
- What happens when ethyl chloride is treated with (i) aqueous ethanolic potassium cyanide and (ii) hot aqueous ethanolic silver nitrite?
- Discuss the mechanisms of nucleophilic substitution reactions, S_N1 and S_N2 .
- Discuss the order of reactivity of primary, secondary and tertiary alkyl halides towards S_N1 and S_N2 mechanisms.
- Discuss the stereochemistry of the products formed through S_N1 mechanism and S_N2 mechanism.
- How does ethyl chloride react sodium ethoxide? What is the name of the reaction?
- Write the reaction products of ethyl chloride with ammonia. Give equations.
- How ethyl acetate is formed from ethyl chloride?
- Write the important uses of ethyl chloride.
- How does ethyl chloride react with (a) NaBr and (b) KI?
- Predict the product obtained by treating ethylchloride with magnesium metal followed by hydrolysis.
- What is Groves process? Give equation.

POLY HALOGEN COMPOUNDS

1.3.1

Chloroform

Pure chloroform is obtained from chloral hydrate

Chloroform decomposes into phosgene in air and light

Chloroform is trichloromethane and its name chloroform was proposed by Dumas as it gives formic acid on hydrolysis.

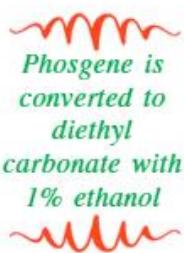
Chloroform is prepared both in the laboratory and on large scale by distilling ethyl alcohol or acetone with bleaching powder and water.

Pure chloroform is obtained by distilling chloral hydrate with concentrated sodium hydroxide solution.



The Chloroform is a colourless, sweet smelling liquid. It is a heavy liquid with density 1.485 g cm^{-3} . It is very slightly soluble in water but soluble in organic solvents such as alcohol, ether, etc.

When exposed to sunlight and air, chloroform decomposes into phosgene and hydrogen chloride.


Phosgene is converted to diethyl carbonate with 1% ethanol



Phosgene is extremely poisonous gas. To use chloroform as an anaesthetic agent, it is necessary to prevent the above reaction. The use of dark brown or amber bottles cuts off active light radiations and filling upto brim keeps out air. Addition of a small amount of 1% ethyl alcohol retards the oxidation and also converts the phosgene formed into harmless diethyl carbonate.

Chloroform is hydrolysed when treated with hot aqueous solution of sodium or potassium hydroxide. The final product formed is sodium or potassium salt of formic acid.

Chloroform is used as a solvent for fats, oils, waxes, rubber, resins, varnishes, iodine, alkaloids, etc. Chloroform is used for the preparation of chloretone (a hypnotic drug), chloropicrin (an insecticide) and as a preservative for anatomical specimens.



P.1.32

Chloroform is treated with aqueous silver nitrate. What happens?

Solution

Pure chloroform does not give precipitate, as the C–Cl bond does not furnish free chloride.

Impure chloroform gives a white silver chloride precipitate.



P.1.33

How do you distinguish between $\text{CH}_3\text{CH}=\text{CHCl}$; $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ and $\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$?

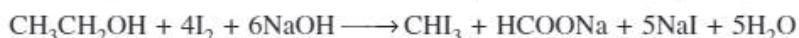
Solution

The Cl in $\text{CH}_2=\text{CHCH}_2\text{Cl}$ is very reactive. This reacts rapidly with AgNO_3 in the cold to give a white precipitate of AgCl . $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ gives white precipitate when warmed with AgNO_3 as it is comparatively less reactive. $\text{CH}_3\text{CH}=\text{CHCl}$ is inert and does not form white precipitate with AgNO_3 .

1.3.2

Iodoform

Iodoform is triiodomethane. Iodoform is prepared by the action of iodine and alkali on ethyl alcohol or acetone. The complete reaction may be written as :



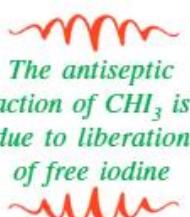
This method is similar to that of chloroform. Sodium carbonate may also be used in place of sodium hydroxide. The complete reaction may be written as :



The compounds of the type RCHXCH_3 (X = halogen) and $\text{RCH}(\text{NH}_2)\text{CH}_3$ can also give iodoform reaction because under the conditions of the reaction, these are initially converted to RCOCH_3 . Lactic acid ($\text{CH}_3\text{CHOHCOOH}$) and pyruvic acid (CH_3COCOOH) also give iodoform reaction.

The following compounds do not give positive iodoform reaction, even though they possess $\text{CH}_3\text{CO}-$ group; $\text{CH}_3\text{COCH}_2\text{COOR}$; $\text{CH}_3\text{COCH}_2\text{NO}_2$; $\text{CH}_3\text{COCH}_2\text{CN}$; $\text{CH}_3\text{COCH}_2\text{COCH}_3$ and CH_3CO (CX=OH, halogen, NH₂ and OR).

Iodoform is an yellow crystalline solid. Iodoform was used earlier as an antiseptic. Its antiseptic action is due to the liberation of free iodine and not due to iodoform itself. Due to its objectionable odour, it has been replaced by other formulations containing iodine.


The antiseptic action of CHI_3 is due to liberation of free iodine

1.3.3**Methylene chloride**

Methylene chloride is dichloromethane. It is widely used as a solvent, a paint remover, a propellant in aerosols and as a process solvent in the manufacture of drugs. It is also used as a metal cleaning and finishing solvent. Chloroform is more toxic and carcinogenic than methylene chloride; it has been replaced by methylene chloride and other solvents in most industrial degreasers and paint removers.

Methylene chloride harms the human central nervous system. Exposure to lower levels of methylene chloride in air can lead to slightly impaired hearing and vision. Higher levels cause dizziness, nausea, tingling and numbness in the fingers and toes. In humans, direct skin contact with methylene chloride causes intense burning and mild redness of the skin. Direct contact with the eyes can burn the cornea.

1.3.4**Carbon tetrachloride**

Carbontetrachloride is prepared by the complete chlorination of methane using excess chlorine in the presence of sunlight.



Carbontetrachloride is manufactured by the action of chlorine on carbon disulphide in the presence of AlCl_3 , FeCl_3 or SbCl_5 as catalyst.



By fractional distillation, CCl_4 can be separated.

Carbon tetrachloride is produced in large quantities for the manufacture of refrigerants, propellants for aerosol cans, in the synthesis of chlorofluorocarbons and pharmaceuticals.

Carbontetrachloride is a colourless, heavy liquid. It is used as solvent for organic reactions. It is because of extra stability to heat that carbontetrachloride is used as a grease remover and fire extinguisher under the name pyrene.

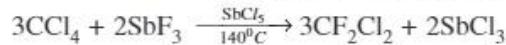
Carbon tetrachloride depletes ozone layer. It is toxic and carcinogenic. So dry cleaners now use 1,1,1-trichloroethane and other solvents instead of carbontetrachloride. It is used as feed stock in the synthesis of chlorofluorocarbons.

Exposure to carbontetrachloride causes liver cancer in humans. The most common effects are dizziness, light headedness, nausea and vomiting. In severe cases, these effects can lead to coma, unconsciousness or even death. It may irritate the eyes on contact or exposure to it may make the heart beat irregular or stop.

1.3.5**Freons**

The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. Some of the derivatives are: CHF_2Cl (monochlorodifluoromethane), CF_2Cl_2 (dichlorodifluoromethane), $\text{HCF}_2\text{CHCl}_2$ (1,1-dichloro-2,2-difluoro ethane) and CF_3Cl (chlorotrifluoromethane) or freon-11.

Freon-12 is manufactured by the reaction of carbontetrachloride with antimony trifluoride at 140°C in the presence of antimony pentachloride as a catalyst.



They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases. The most important and useful derivative is CF_2Cl_2 which is commonly known as freon or freon-12. It is manufactured from tetrachloromethane by Swarts reaction. It can be easily liquefied and chemically inert.

*Under the name
pyrene, CCl_4 is
used as fire
extinguisher*

*Freons deplete
ozone layer*

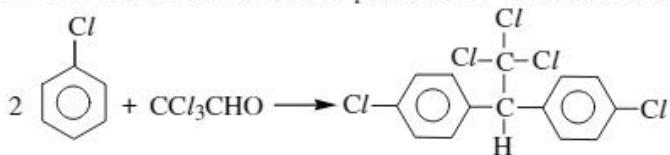

D.D.T. is
dichlorodiphenyl-
trichloroethane


Freons are used for aerosol propellants, refrigeration and air conditioning purposes. Since freons have been found to be one of the factors responsible for the depletion of ozone layer, they are being replaced by other harmless compounds. In refrigerators and automotive air conditioners, Freon-12 has been replaced by Freon-22, CHClF_2 . Freons with C–H bonds (such as Freon-22), called HCFCs, are generally destroyed at lower altitudes before they reach the stratosphere. HCFC-123 (CHCl_2CF_3) is used as a substitute for Freon-11 in making plastic foams.

1.3.6

D.D.T.

D.D.T. is p,p'-dichlorodiphenyl trichloroethane. Its IUPAC name is 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane. It is prepared by heating a mixture of chlalor and chlorobenzene in the presence of concentrated sulphuric acid.



It is the first chlorinated organic insecticide, it has high chemical stability and a powerful insecticide, particularly very effective against anopheles mosquitoes which spread malaria. DDT is not metabolised very rapidly by animals, instead, it is deposited and stored in the fatty tissues. It is highly toxic to fish. D.D.T. showed undesired side effects. It is a long-lasting insecticide and its residues accumulate in the environment. In 1972, D.D.T. was banned by the U.S. Environmental Protection Agency for use as an agricultural insecticide. It is still used as a last resort, however, in countries where insect-borne diseases threaten human life.



P.1.34 How iodoform is distinguished from chloroform?

Solution Chloroform is a sweet smelling colourless liquid while iodoform is a yellow crystalline solid having a pungent characteristic smell.

Iodoform gives yellow precipitate with silver nitrate solution. Chloroform does not give precipitate with silver nitrate solution.



P.1.35 How will you distinguish between chloroform and carbontetrachloride?

Solution Chloroform gives carbylamine when heated with aniline and alcoholic potassium hydroxide, whose smell is very offensive. Carbontetrachloride does not give this test.



P.1.36 What is teflon? How is it prepared?

Solution Teflon is polytetrafluoro ethylene. It is prepared by the action of chloroform with antimony trifluoride and hydrofluoric acid, followed by vinyl polymerisation.



P.1.37 What are freons ? How are they prepared ?

Solution Chlorofluorocarbon compounds are called freons. Dichlorodifluoromethane is commonly called freon12. It is prepared by the reaction of antimony trifluoride on carbontetrachloride at 140°C using antimony pentachloride as catalyst.

EXERCISE - 1.1.3

- Give the toxic effects of polyhalogen compounds.
- Write the series of reactions of chloroform with hot aqueous solution of potassium hydroxide.
- Write notes on carbylamine reaction and Reimer-Tiemann reaction.
- Give important uses and tests for chloroform.
- Write a note on freons
- How are the following prepared? Write their uses.
(a) CHI_3 , (b) CH_2Cl_2 , (c) CCl_4 and (d) CF_2Cl_2 .
- Write a note on D.D.T.
- Which is non-biodegradable polyhalogen compound?

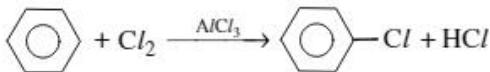
ARYL HALIDES

Chlorobenzene is the important aryl halide. Preparation and properties of chlorobenzene are mainly discussed here.

1.4.1**Preparation**

Preparation of halobenzenes from phenol by reaction with hydrogen halides, phosphorus halides or thionyl halides is difficult, because carbon–oxygen bond in phenols has partial double bond character.

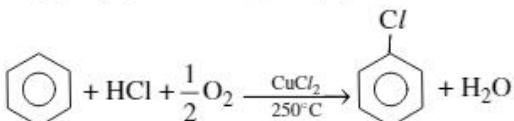
From benzene : In presence of a Lewis acid such as FeCl_3 or AlCl_3 , benzene reacts with chlorine to form chlorobenzene.



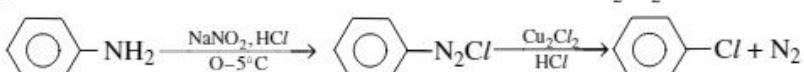
With bromine, under similar conditions, bromobenzene is formed. Fluorobenzene cannot be prepared by this method because of the high affinity of fluorine for hydrogen. Reaction with iodine is reversible and HI formed should be immediately oxidised by using nitric acid or periodic acid.

Toluene on chlorination in dark in the presence of iron or ferric chloride catalyst gives a mixture of orthochlorotoluene and parachlorotoluene. This mixture can be separated based on the difference in melting points of the isomeric chlorotoluenes.

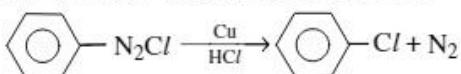
From benzene by Raschig Process : Chlorobenzene is manufactured from benzene in which a mixture of benzene vapour, hydrogen chloride and air is passed over copper (II) chloride (catalyst) at 250°C .



From diazonium compounds : The most convenient method of preparing chlorobenzene in laboratory is by **Sandmeyer's reaction**, in which benzene diazonium chloride obtained from aniline is heated with cuprous chloride in presence of hydrochloric acid. Bromobenzene is formed, with Cu_2Br_2 and HBr .

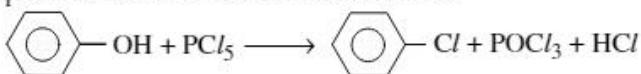


If copper powder and HCl or HBr is used, instead of Cu_2Cl_2 or Cu_2Br_2 , the reaction is called **Gattermann reaction**.



Iodobenzene can be obtained by warming of benzene diazonium salt with KI . Fluorobenzene can be obtained by the reaction of benzene diazonium chloride with fluoboric acid, followed by heating the diazonium fluoroborate salt (**Shiemann's reaction**).

From phenol : Chlorobenzene can be prepared by the action of phosphorus pentachloride on phenol. The yield is poor. To get better yield, a little of triphenyl phosphate is added to the reaction mixture.



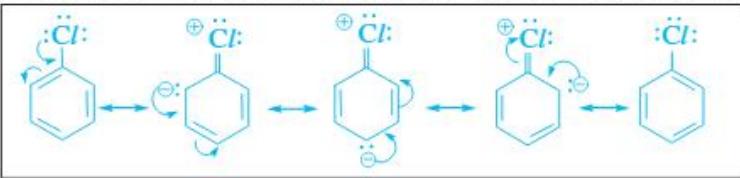
1.4.2

Chemical properties Nucleophilic substitution

Aryl halides are much less reactive towards nucleophilic substitution reactions than alkyl halides. The less reactivity of aryl halides is due to the following reasons:

a) Withdrawal of electrons by benzene nucleus and stabilisation by resonance

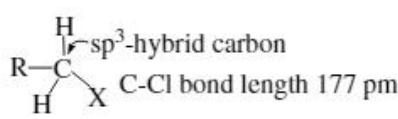
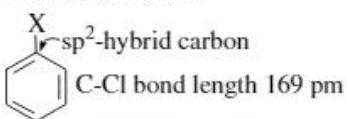
In aryl halides, the electron pairs on halogen atom are in conjugation with π electrons of the ring and the following resonance hybrid structures are possible.



The resonance hybrid structure indicates that $C-Cl$ bond has partial double bond character. As a result, the $C-Cl$ bond in chlorobenzene (halobenzene) is shorter and hence stronger as compared to that in alkyl halides. Thus, cleavage of $C-Cl$ bond becomes difficult which makes it less reactive towards nucleophilic substitution reaction.

b) Hybridisation of carbon atom of C-X bond

In haloalkanes, the carbon atom bearing halogen is sp^3 hybridised while in case of haloarene, the carbon atom bearing halogen is sp^2 hybridised. The sp^2 hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of C-X bond more tightly than sp^3 hybridised carbon in haloalkane with less s-character.



c) Polarity of C-X bond

The C-X bond in haloalkanes is more polar than the C-X bond in haloarenes. Greater the polarity of the bond, more is the reactivity. Lower polarity of C-X bond in aryl halides is due to the fact that electron withdrawing inductive effect of halogen is opposed by the electron releasing resonance effect, as is evident from the positive charge on halogen in the middle resonance structures.

d) Instability of phenyl cation

In case of aryl halides, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore, S_N1 mechanism is ruled out.

Aryl halides are much less reactive than alkyl halides towards nucleophilic substitution

e) Electron rich arenes

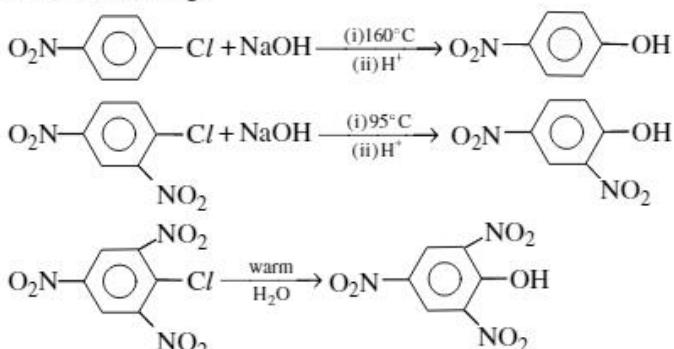
Phenol is manufactured from chlorobenzene by Dow's process

Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

Replacement by hydroxyl group : On heating chlorobenzene with an aqueous solution of NaOH at 350°C under 300 atmosphere pressure, sodium phenoxide is formed which on subsequent acidification produces phenol. This reaction is used in the Dow's process for the manufacture of phenol.



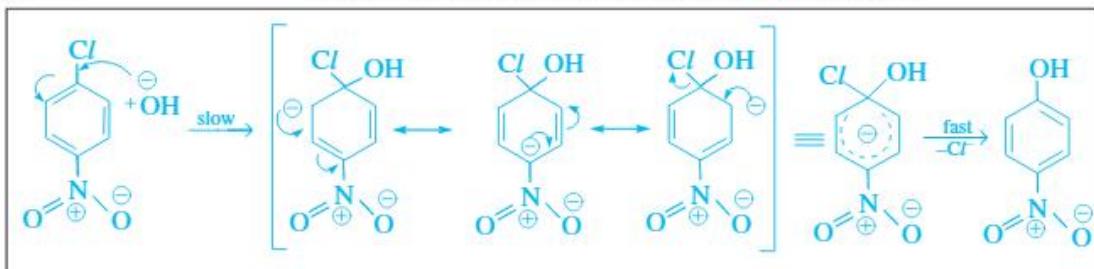
The reactivity of aryl halides towards nucleophilic substitution reaction increases if some electron withdrawing group such as nitro, cyano, aldehyde, carboxyl group is attached to the ring.



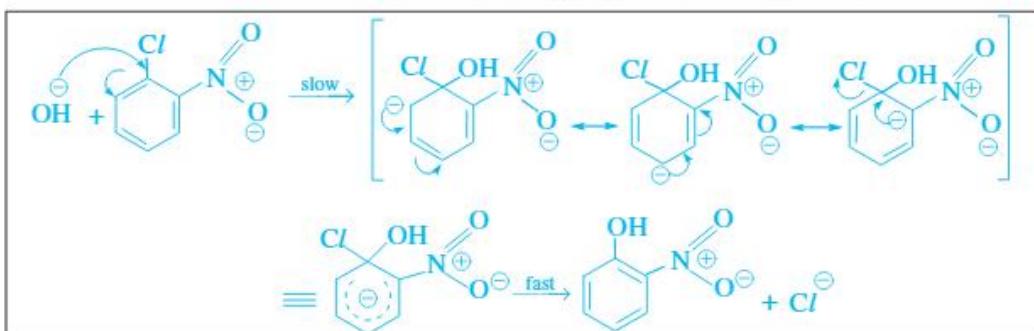
Reactivity will be more if number of $-\text{NO}_2$ groups attached is more

Thus, we observe that as the number of electron withdrawing groups increases, the reactivity increases. The effect is pronounced when electron withdrawing group is introduced at ortho and para positions. However, no effect on reactivity of haloarenes is observed by the presence of electron withdrawing group at meta position.

Mechanism, when nitro group is at para position

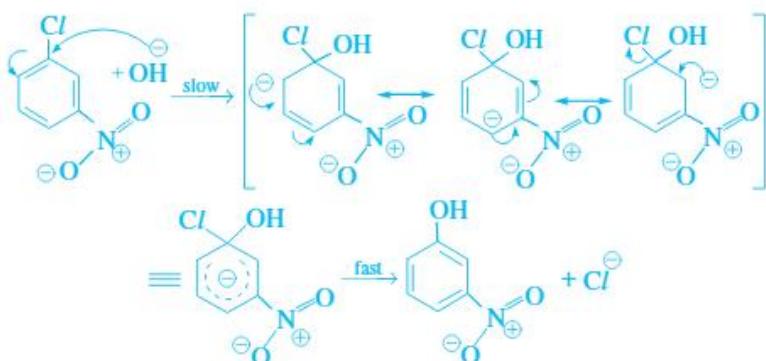


Mechanism, when nitro group is at ortho position



No effect on reactivity of haloarenes when electron withdrawing group is at meta position

Mechanism, when nitro group is at meta position



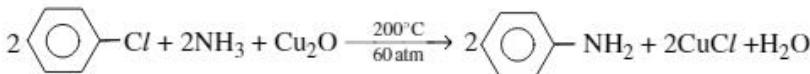
The presence of nitro group at ortho and para positions withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene. The carbanion thus formed is stabilised through resonance.

The negative charge appeared at ortho and para positions with respect to the halogen substituent is stabilised by $-\text{NO}_2$ group while in case of meta-nitro chlorobenzene, none of the resonating structures bears the negative charge on carbon atom bearing the $-\text{NO}_2$ group. Therefore, the presence of nitro group at meta-position does not stabilise the negative charge and no effect on reactivity is observed.

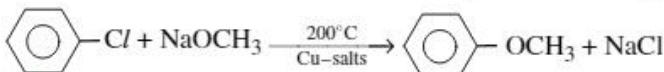
Replacement by cyano group : When heated with cuprous cyanide in the presence of pyridine or dimethyl formamide at 200°C , chlorobenzene gives cyanobenzene.



Replacement by amino group : Halogen atom of haloarenes is replaced by amino group by reacting with aqueous ammonia at 200°C under pressure and in presence of catalyst cuprous oxide.

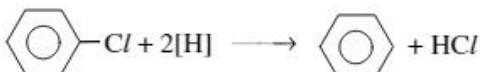


Replacement by methoxy group : Anisole is formed when chlorobenzene is heated with sodium methoxide at 200°C in presence of copper salts.



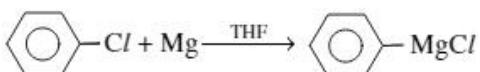
Reduction

Chlorobenzene is reduced to benzene with lithium aluminium hydride or Ni-Al alloy in sodium hydroxide solution.



Reaction with metals

Chlorobenzene forms Grignard reagent with magnesium in tetrahydrofuran as solvent.



Formation of alkyl arene from alkyl halide and aryl halide is called Wurtz–Fittig reaction

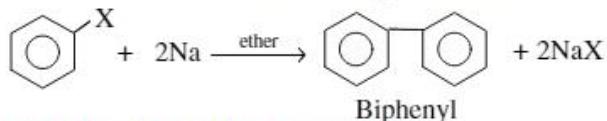
Halogen atom in aryl halide is *o*-and *p*-directing but slightly deactivating

In electrophilic substitution of chlorobenzene, para substituted product is the major product

The formation of alkylarene when a mixture of an alkyl halide and aryl halide is treated with sodium in dry ether is called **Wurtz–Fittig reaction**. By this reaction, toluene is formed from chlorobenzene.

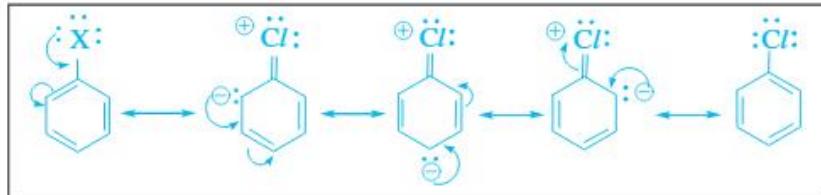


Aryl halides when treated with sodium in dry ether, analogous compounds are formed. This reaction is called **Fittig reaction**.



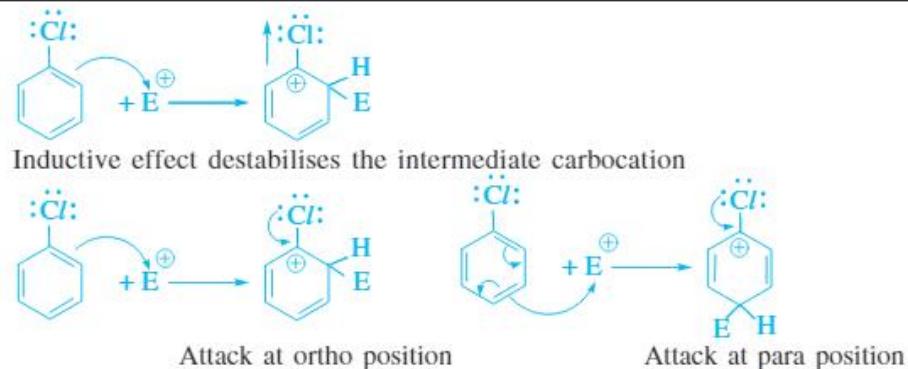
Electrophilic substitution reactions

Haloarenes undergo the usual electrophilic substitution reactions in the benzene ring such as nitration, halogenation, sulphonation and Friedel–Crafts reactions. Though slightly deactivating, halogen atom in the ring is *o*–, *p*– directing; therefore, further substitution occurs at ortho and para positions to the halogen atom. The resonating structures of chlorobenzene are given here.



Due to resonance, the electron density increases more at ortho and para positions than at meta position. Further, due to $-I$ effect of halogen, it has a tendency to withdraw electrons from the benzene ring. As a result, the ring gets deactivated as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.

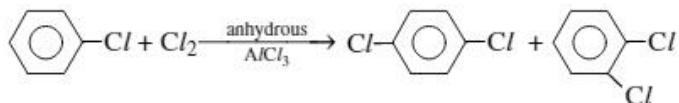
Chlorine withdraws electrons through inductive effect and releases electrons through resonance. Through inductive effect, chlorine destabilises the intermediate carbocation formed during the electrophilic substitution. Through resonance, halogen tends to stabilise the carbocation.



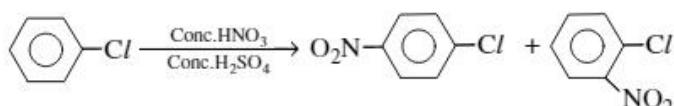
The inductive effect causes net electron withdrawal and thus leads to net deactivation. The resonance effect tends to oppose the inductive effect for the attack at ortho and para positions and hence makes the deactivation less for ortho and para attack. Reactivity is thus controlled by the stronger inductive effect and orientation is controlled by resonance effect.

Formation of alkyl arene from alkyl halide and aryl halide is called Wurtz-Fittig reaction

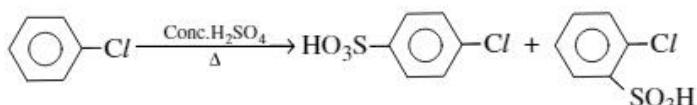
Halogenation : Halogenation takes place in presence of iron or ferric chloride or anhydrous aluminium chloride as catalyst. The major product formed is 1,4-dichloro-benzene and the minor product is 1,2-dichlorobenzene.



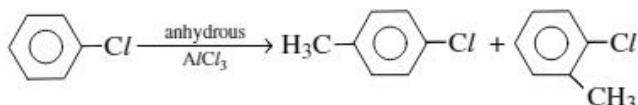
Nitration : When chlorobenzene is heated with a mixture of conc. nitric acid and conc. sulphuric acid, the major product is 1-chloro-4-nitrobenzene and the minor product is 1-chloro-2-nitrobenzene.



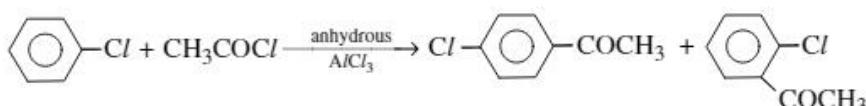
Sulphonation : Heating with concentrated sulphuric acid, chlorobenzene gives 4-chlorobenzene sulphonic acid as major product and 2-chlorobenzene sulphonic acid as the minor product.



Friedel-Craft's alkylation : In presence of anhydrous aluminium chloride, chlorobenzene reacts with methyl chloride to give 1-chloro-4-methylbenzene as the major product and 1-chloro-2-methylbenzene as the minor product.



Friedel-Craft's acylation : In presence of anhydrous aluminium chloride, chlorobenzene reacts with acetyl chloride to give 4-chloroacetophenone as the major product and 2-chloroacetophenone as the minor product.



Uses of chlorobenzene : Chlorobenzene is used for the manufacture of aniline, phenol, biphenyl, nitrobenzene, picric acid, DDT, etc.



P.1.38

Among the three isomeric dichlorobenzenes, which has the highest boiling point and highest melting point ?

Solution

Boiling point of o- dichlorobenzene is greater than the boiling point of m- and p- dichlorobenzenes due to its greater polar nature.

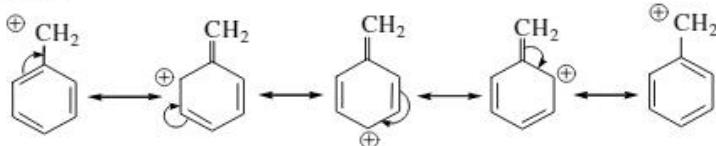
Boiling point order is : o- > m- > p- dichlorobenzene. Melting points of p- dichlorobenzene is greater than that of o- and m- dichlorobenzenes. It is due to symmetry of para- isomer of dichlorobenzene that fits in crystal lattice better as compared to o- and m- isomers.

Melting points decrease in the order : p- > o- > m- dichlorobenzene



P.1.39 Benzyl chloride undergoes nucleophilic substitution much more easily than chlorobenzene. Explain.

Solution Benzyl chloride undergoes nucleophilic substitution readily via resonance stabilised benzyl carbocation.



On the other hand C–Cl bond in benzene has partial double bond character due to resonance and hence is difficult to cleave.

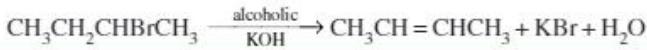
Hence, benzyl chloride undergoes nucleophilic substitution much more easily than chlorobenzene.



P.1.40 Which product will form when optically active form of C_4H_9Br is subjected to dehydrohalogenation?

Solution The optically active form of C_4H_9Br is $CH_3CH_2CHBrCH_3$.

2–Bromobutane on dehydrohalogenation gives 2-butene according to Saytzeff rule.



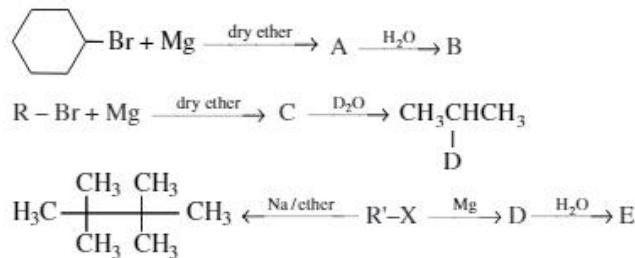
P.1.41 Nucleophilic substitution in aryl halides is facilitated by electron withdrawing groups while electrophilic substitution is facilitated by electron releasing groups. Why?

Solution Nucleophilic substitution in aryl halides takes place via carbanion as intermediate, which are stabilised by electron withdrawing groups.

Electrophilic substitution takes place through carbocations as intermediates, which are stabilised by electron releasing groups. The rate of the reaction increases if the intermediate involved in this reaction is stabilised.



P.1.42 Identify A, B, C, D, E, R and R' in the following.



Solution A : ; B : ; R : $(\text{CH}_3)_2\text{OH}-$; C : $(\text{CH}_3)_2\text{CHMgBr}$; R' – $(\text{CH}_3)_3\text{C}-$; D : $(\text{CH}_3)_3\text{C MgBr}$ and E : $(\text{CH}_3)_3\text{CH}$



P.1.43 What happens when iodobenzene is heated with copper powder at 200°C ?

Solution When iodobenzene is heated with Cu powder at 200°C in a sealed tube, biphenyl is formed.



This is called Ullmann reaction

Aryl chlorides and bromides usually do not give this reaction unless the halogen is activated by suitable substituents ($-\text{NO}_2$) in the ortho or para position.

EXERCISE - 1.1.4

1. How chlorobenzene is prepared from (i) aniline and (ii) phenol?
2. How phenol is obtained from chlorobenzene?
3. Discuss the effect of nitro group in chlorobenzene towards nucleophilic substitution reaction.
4. Describe with suitable examples the Wurtz-Fittig reaction and Fittig reaction.
5. Discuss the electrophilic substitution reactions of chlorobenzene.
6. Compare the reactivity of benzene and chlorobenzene towards electrophilic substitution reactions.
7. How is iodobenzene prepared?
8. Give two uses of chlorobenzene.

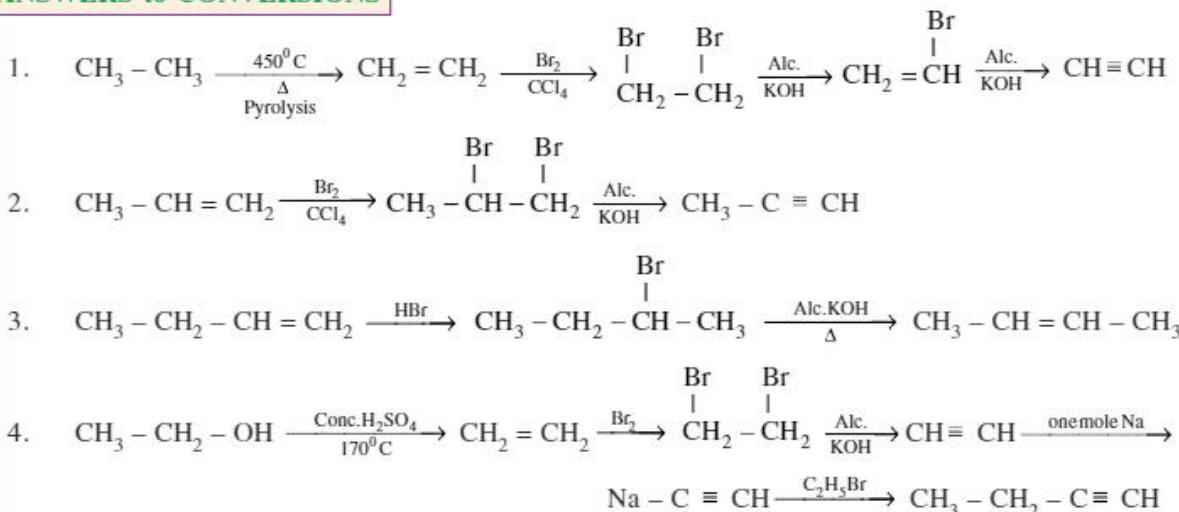


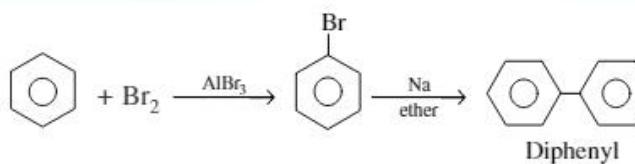
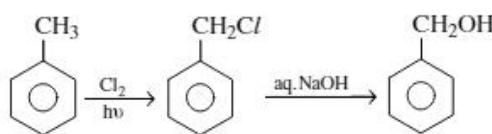
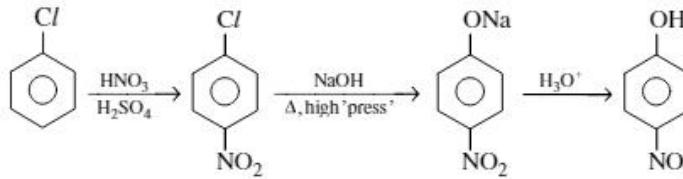
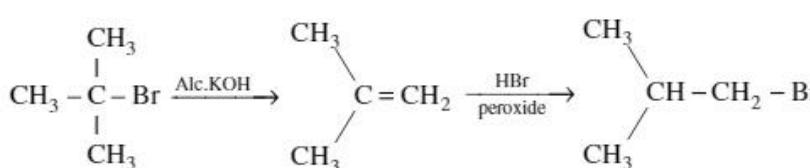
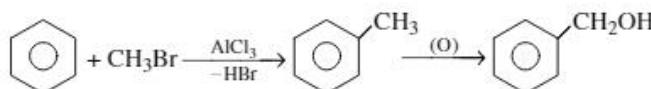
1. Depending upon the number of halogen atoms present in the structure, alkyl or aryl halides are classified as mono, di, tri or poly halogen compounds.
2. Alkyl halides are also classified as primary, secondary or tertiary depending upon the type of carbon to which halogen is attached.
3. The halogen atom of alkyl halide carries partial negative charge and carbon carries partial positive charge. The polarity of carbon-halogen bond of alkyl halides is responsible for their nucleophilic substitution, elimination and their reaction with metals.
4. Alkyl halides are prepared by the reaction of halogen acids or phosphorous halides or thionyl chloride with alcohols.
5. Alkyl halides are also prepared by the free radical halogenation of alkanes or by the addition of halogen acids to alkenes. Alkyl iodides can be prepared by halide exchange reaction.
6. The boiling points of alkyl halides are slightly higher than the corresponding hydrocarbons or ethers due to strong dipole-dipole interactions and van der Waals forces of attraction but lower than the corresponding alcohols and carboxylic acids.
7. Based on the kinetic properties, nucleophilic substitution reactions are categorised as S_N1 and S_N2 type.
8. The order of reactivity of S_N1 reactions is $3^\circ > 2^\circ > 1^\circ >$ methyl. S_N1 reactions are characterised by recemisation.
9. The order of reactivity of S_N2 reactions is methyl $> 1^\circ > 2^\circ > 3^\circ$. S_N2 reactions of chiral alkyl halides are characterised by the inversion of configuration.

10. Alcohols are formed from alkyl halides by hydrolysis with aqueous sodium or potassium hydroxide or moist silver oxide.
11. Alcoholic potassium cyanide reacts with alkyl halides to give alkyl cyanides and alcoholic silver cyanide reacts to give alkyl isocyanides as major products.
12. Alkyl halides react with sodium or potassium nitrite to give alkyl nitrite as the major product whereas silver nitrite gives nitro alkane as major product.
13. Ethers are formed by Williamson synthesis from alkyl halides and sodium alkoxide.
14. A mixture of amines and quaternary salt are formed when alkyl halides react with ammonia.
15. When alkyl halides react with alcoholic potassium hydroxide, alkenes are formed and the products formed depend upon Saytzeff rule.
16. Alkyl halides react with metals like sodium, magnesium, lithium, zinc, etc. They are reduced to alkanes with nascent hydrogen.
17. Chloroform is obtained by the reaction of bleaching powder with ethyl alcohol or acetone.
18. Chloroform undergoes atmospheric oxidation to poisonous carbonyl chloride.
19. With nitric acid, chloroform forms chloropicrin, used as an insecticide.
20. Chloroform is hydrolysed to sodium or potassium salt of formic acid with hot aqueous sodium or potassium hydroxide.
21. In Reimer-Tiemann reaction, chloroform reacts with phenol in presence of alkali to give salicylaldehyde.
22. Carbylamine reaction is the reaction between a primary amine, chloroform and alcoholic potassium hydroxide.
23. Iodoform is prepared by the reaction of ethyl alcohol or acetone with iodine and alkali.
24. Freons are chlorofluorocarbon compounds of methane and ethane. They are used for aerosol propellants and also for refrigeration.
25. Sandmeyer's reaction is used in the preparation of chlorobenzene from benzene diazonium chloride with cuprous chloride.
26. The formation of chlorobenzene from benzene diazonium chloride and copper metal in presence of hydrochloric acid is called Gattermann reaction.
27. Aryl halides are much less reactive towards nucleophilic substitution reactions than alkyl halides.
28. Chlorine atom in chlorobenzene can be replaced by hydroxyl group, cyano group, amino group and methoxy group.
29. Wurtz-Fittig reaction is the reaction between aryl halide and alkyl halide in presence of sodium to form alkylarene. In Fittig reaction, biphenyl is formed from phenyl halide.
30. Chlorobenzene undergoes electrophilic substitution reactions. Chlorine atom in chlorobenzene is ortho and para directing and slightly deactivates benzene ring.

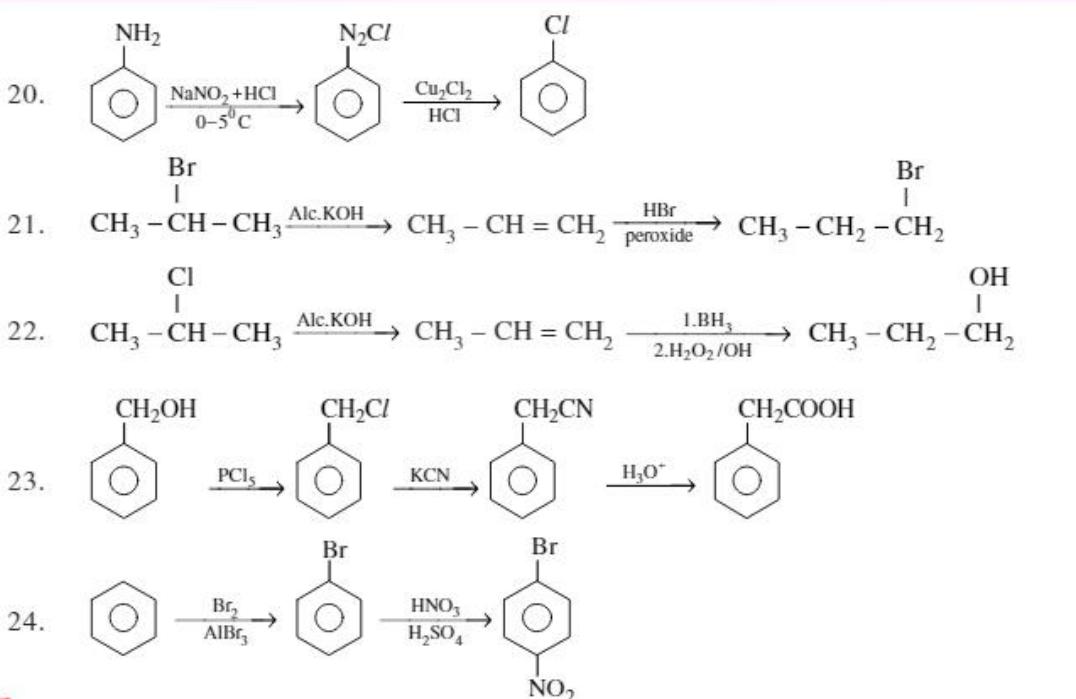
CONVERSIONS

1. Ethane to bromoethene
2. Propene to propyne
3. But-1-ene to but-2-ene
4. Ethanol to 1-butyne
5. Benzene to biphenyl
6. 1-iodo butane to n-octane
7. Methyl bromide to propanone
8. Toluene to benzyl alcohol
9. Propene to nitropropane
10. Ethyl alcohol to ethyl fluoride
11. Propene to 1-propanol
12. But-1-ene to 1-iodo butane
13. Ethanol to propane nitrile
14. Chloroethane to butane
15. Chlorobenzene to p-nitrophenol
16. n-Propyl bromide to isopropyl bromide
17. tert-Butyl bromide to isobutyl bromide
18. Toluene to benzyl alcohol
19. 2-Methyl-1-propene to 2-chloro-2-methyl propane
20. Aniline to chlorobenzene
21. Isopropyl bromide to n-propyl bromide
22. 2-Chloropropane to 1-propanol
23. Benzyl alcohol to 2-phenylethanoic acid
24. Benzene to 4-bromonitrobenzene

ANSWERS to CONVERSIONS

5.  (This is Fitting Reaction)
6. $2\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{I} + 2\text{Na} \xrightarrow{\text{ether}} \text{CH}_3 - (\text{CH}_2)_6 \text{CH}_3$
7. $\text{CH}_3\text{-Br} \xrightarrow{\text{KCN}} \text{CH}_3 - \text{CN} \xrightarrow{\text{H}_3\text{O}^+} \text{CH}_3\text{COOH} \xrightarrow{\text{Ca}} (\text{CH}_3\text{COO})_2\text{Ca} \xrightarrow{\text{distillation}} \text{CH}_3\text{COCH}_3$
8. 
9. $\text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow[\text{peroxide}]{\text{HBr}} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{Br} \xrightarrow{\text{AgNO}_2} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{NO}_2$
10. $\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{PCl}_5} \text{C}_2\text{H}_5\text{Cl} \xrightarrow[\text{acetone}]{\text{AgF}} \text{C}_2\text{H}_5\text{F}$
11. $\text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow[2.\text{H}_2\text{O}_2/\text{OH}^-]{1.\text{BH}_3} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$
12. $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2 \xrightarrow[\text{peroxide}]{\text{HBr}} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \overset{\text{Br}}{\underset{|}{\text{CH}_2}} \xrightarrow[\text{Acetone}]{\text{KI}} \text{CH}_3 - \overset{\text{I}}{\underset{|}{\text{CH}_2}} - \text{CH}_2 - \overset{\text{I}}{\underset{|}{\text{CH}_2}}$
13. $\text{CH}_3 - \text{CH}_2 - \text{OH} \xrightarrow{\text{PCl}_5} \text{CH}_3 - \text{CH}_2 - \text{Cl} \xrightarrow{\text{KCN}} \text{CH}_3 - \text{CH}_2 - \text{CN}$
14. $2\text{CH}_3 - \text{CH}_2 - \text{Cl} + 2\text{Na} \xrightarrow{\text{dry ether}} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$
15. 
16. $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{Br} \xrightarrow{\text{Alc.KOH}} \text{CH}_3 - \text{CH} = \text{Br} \xrightarrow{\text{HBr}} \text{CH}_3 - \overset{\text{Br}}{\underset{|}{\text{CH}}} - \text{CH}_3$
17. 
18. 
19. $\text{CH}_3 - \overset{\text{CH}_3}{\underset{|}{\text{C}}} = \text{CH}_2 \xrightarrow{\text{HCl}} \text{CH}_3 - \overset{\text{CH}_3}{\underset{|}{\text{C}}} - \text{CH}_3$

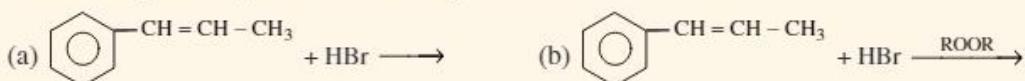
CHEMISTRY IIB



EXERCISE - 1.2

- Explain the hybridisation of carbon to which halogen atom is attached in alkyl halides, vinyl halides, aryl halides and arylalkyl halides.
- Differentiate between aryl halides and arylalkyl halides.
- Write the common names and IUPAC names of all isomers of the formula, C_4H_9Cl .
- Write all the possible structural isomers with the formula, $C_5H_{11}Br$.
- Give the bond line structures of (i) Allyl chloride (ii) Butylene chloride and (iii) 2-chloro-2-phenylbutane.
- How ethyl bromide is formed by Hunsdiecker reaction?
- How do the boiling points vary in alkyl halides with increase in the size of the alkyl group for the given halide and also of the halide for the given alkyl group?
- Ethyl chloride is more reactive than vinyl chloride towards nucleophilic substitution. Explain.
- Give the nucleophilic substitution mechanism with allylic and benzylic halides?
- What happens when an optically active alkyl halide undergoes nucleophilic substitution?
- Why S_N1 reactions are favourable in polar solvents?
- Differentiate between nucleophilicity and basicity with suitable examples.
- Explain Saytzeff rule with suitable examples.
- Write a note on elimination reactions of alkyl halides.
- How the formation of poisonous phosgene can be prevented from chloroform?
- What are the consequences when human beings are exposed to carbon tetrachloride?
- In aqueous potassium hydroxide nucleophilic substitution takes place, however in alcoholic potassium hydroxide elimination takes place. Account for the observation with suitable example.

18. Discuss the effect of the nucleophile and substrate on the mechanism of nucleophilic substitution.
19. Which test is useful to distinguish between 2-pentanone and 3-pentanone?
20. Electron withdrawing groups in benzene ring facilitate nucleophilic substitution. Substantiate.
21. What are the disadvantages of freons?
22. Give the IUPAC name of D.D.T. Why is it banned in some countries?
23. Give the equation for the formation of chlorobenzene by Raschig method.
24. Halogen atom present in benzene ring is ortho, para directing, but deactivating. Why?
25. Predict the product(s) of the following reaction.



26. Tertiary halides mainly undergo elimination rather than substitution. Justify.
27. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{PBr}_3} \text{A} \xrightarrow[\text{alcoholic KOH}]{\text{CH}_3\text{CHO}} \text{B} \xrightarrow{\text{HBr}} \text{C} \xrightarrow{\text{NH}_3} \text{D}$. Write the formula of the final product D. (Ans : $\text{CH}_3\text{CHNH}_2\text{CH}_3$)
28. $(\text{CH}_3)_3\text{CC}(\text{CH}_3)_3 \xleftarrow{\text{Na, ether}} \text{R}'-\text{X} \xrightarrow{\text{Mg}} \text{D} \xrightarrow{\text{H}_2\text{O}} \text{E}$. What is E? (Ans : isobutane)
29. $\text{CH}_3\text{CH}_2\text{MgBr} \xrightarrow[\text{H}_2\text{O}]{\text{CH}_3\text{CHO}} \text{X} \xrightarrow{\text{HBr}} \text{Y}$. Write the product obtained when compound Y is subjected to dehydrohalogenation. (Ans : $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$)
30. $\text{CH}_3\text{CH}_2\text{CH}_2\text{I} \xrightarrow{\text{alc.KOH}} \text{A} \xrightarrow{\text{H}^+, \text{H}_2\text{O}} \text{B} \xrightarrow{\text{SOCl}_2} \text{C} \xrightarrow[\text{LiAlH}_4]{[\text{H}]} \text{D}$. Write the molecular weight of compound D. (Ans : 44)
31. An unsaturated hydrocarbon, C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound, $\text{C}_5\text{H}_9\text{Cl}$ in bright sunlight. Predict that hydrocarbon.
32. $\text{CH}_3\text{CHBrCH}_3 \xrightarrow{\text{alc.KOH}} \text{A} \xrightarrow[\text{peroxide}]{\text{HBr}} \text{B} \xrightarrow[\text{acetone}]{\text{NaI}} \text{C}$. Write the positional isomer of compound C. (Ans : Isopropyl iodide)
33. $\text{C}_4\text{H}_9\text{Br}$ (A) is a primary alkyl halide, which on reaction with alcoholic KOH gives a compound (B). Compound (B) on reaction with HBr gives compound (C). (C) is an isomer of (A). When (A) reacts with sodium metal, compound (D) is formed. Molecular formula of compound (D) is C_8H_{18} which is different from the compound formed when n-butyl bromide is reacted with sodium. Starting from the structural formula of (A), write equations for all the reactions.
34. Predict the order of reactivity of the following compounds towards nucleophilic substitution.

