

HALOALKANES AND HALOARENES

10.1 Classification :

Q. What are uses of organic compound containing halogen ?

Solution : Chlorine containing antibiotic, chloramphenicol, produced by soil microorganisms is very effective for the treatment of typhoid fever. Our body produces iodine containing hormone, thyroxine, the deficiency of which cause a disease called goiter. Synthetic halogen compounds, viz. chloroquine is used for the treatment of malaria; halothane is used as an anaesthetic during surgery. Certain fully fluorinated compounds are being considered as potential blood substitutes in surgery.

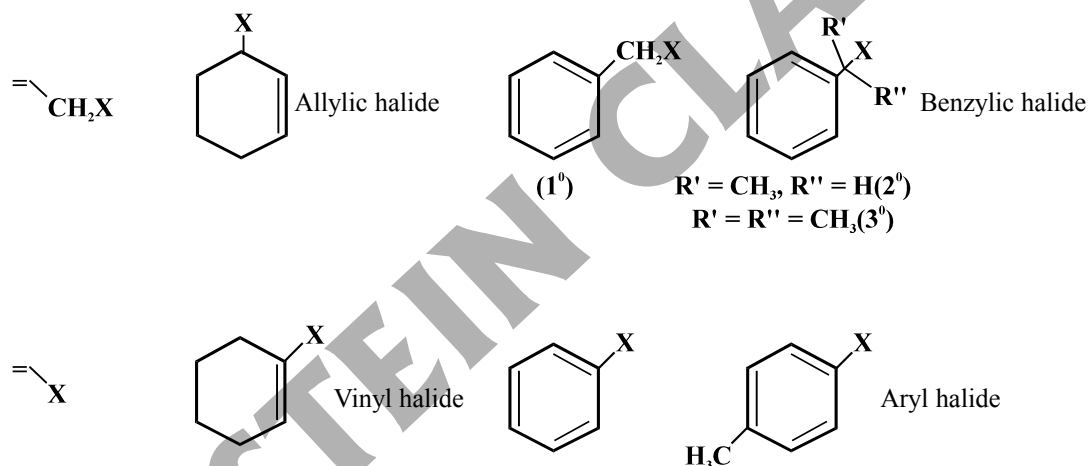
Q. What are Allylic halides, Benzylic halides, Vinylic halides and Aryl halides ?

Solution : Allylic Halide : These are the compounds in which the halogen atom is bonded to an sp^3 -hybridised carbon atom next to carbon-carbon double bond ($C = C$) i.e. to an allylic carbon.

Benzylic halide : These are the compounds in which the halogen atom is bonded to an sp^3 -hybridised carbon atom next to an aromatic ring.

Vinylic halide : These are the compounds in which the halogen atom is bonded to an sp^2 -hybridised carbon atom of a carbon-carbon double bond ($C = C$).

Aryl halide : These are the compounds in which the halogen atom is bonded to the sp^2 -hybridised carbon atom of an aromatic ring.



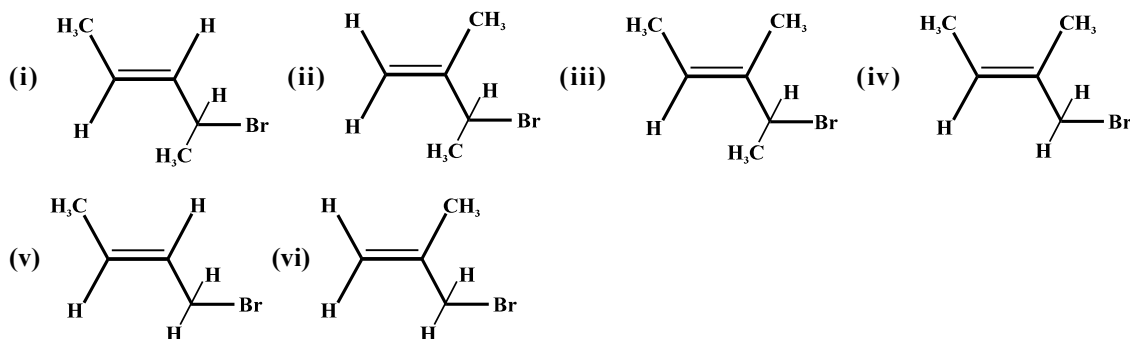
10.2 Nomenclature :

Q. Draw the structures of all the eight structural isomers that have the molecular formula $C_5H_{11}Br$. Name each isomer according to IUPAC system and classify them as primary, secondary or tertiary bromide. [NCERT Solved Example 10.1]

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°)

Q. Write IUPAC names of the following :



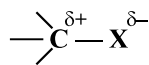
Solution : (i) 4-Bromopent-2-ene (ii) 3-Bromo-2-methylbut-1-ene (iii) 4-Bromo-3-methylpent-2-ene (iv) 1-Bromo-2-methylbut-2-ene (v) 1-Bromobut-2-ene (vi) 3-Bromo-2-methylpropene.

Q. Write structures of the following compounds; (i) 2-Chloro-3-methylpentane (ii) 1-Chloro-4-ethylcyclohexane (iii) 4-tert. Butyl-3-iodoheptane (iv) 1,4-Dibromobut-2-ene (v) 1-Bromo-4-sec. butyl-2-methylbenzene.

10.3 Nature of C–X bond :

Q. What is the nature of C-X bond ?

Solution : Halogen atoms are more electronegative than carbon, the carbon-halogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.



The size of halogen atom increases as we go down the group. Fluorine atom is the smallest and iodine atom, the largest. Consequently the carbon-halogen bond length also increases from C–F to C–I.

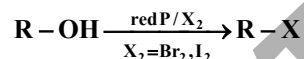
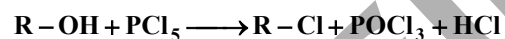
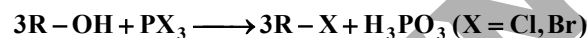
10.4 Method of Preparation :

Q. What are the different method of preparation of alkyl halide from alcohols ?

Solution : (i) $\text{R-OH} + \text{HX} \xrightarrow{\text{ZnCl}_2} \text{R-X} + \text{H}_2\text{O}$

The reactions of primary and secondary alcohols with HX require the presence of a catalyst, ZnCl_2 . With tertiary alcohols, the reaction is conducted by simply shaking with concentrated HCl at room temperature. Constant boiling with HBr (48%) is used for preparing alkyl bromide. Good yields of R–I may be obtained by heating alcohols with sodium or potassium iodide in 95% phosphoric acid. The order of reactivity of alcohols with a given haloacid is $3^\circ > 2^\circ > 1^\circ$. Decreasing order of reactivity of halogen acid with given alcohol is $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$.

(ii) Formation of alkyl halide takes place by reacting the phosphorus halides.

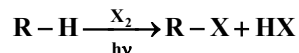


(iii) Formation of alkyl halide from thionyl chloride is preferred because the other two products are escapable gases.



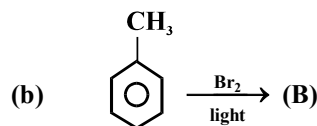
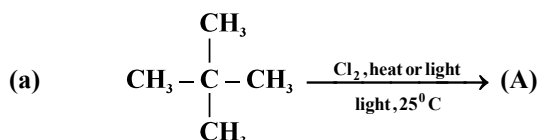
Q. How the alkyl halide is prepared from alkane ?

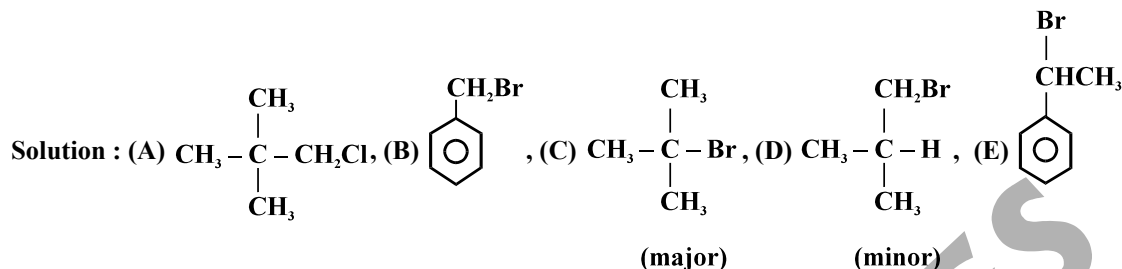
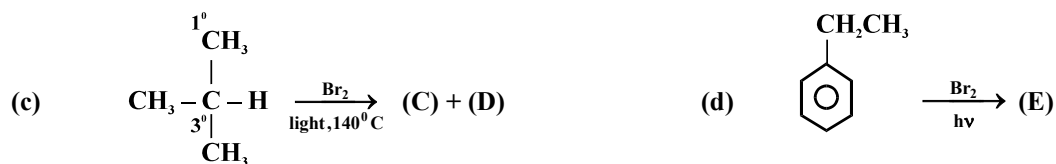
Solution : By halogenation of hydrocarbons formation of alkyl halide takes place. It is a free radical substitution reaction. Free radical chlorination or bromination of alkanes gives a complex mixture of isomeric mono- and polyhaloalkanes, which is difficult to separate as pure compounds. Consequently, the yield of any one compound is low.



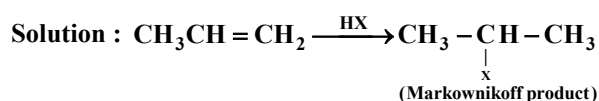
Decreasing order of reactivity of X_2 is $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

Q. Identify (A), (B), (C), (D) and (E) in the following reactions.





Q. Explain the formation of alkyl halide from alkene by reacting with halogen acid.



Q. Why phenol cannot be used for the preparation of aryl halide by reacting with halogen acid ?

Solution : Phenol cannot be used for the preparation of aryl halide because the carbon-oxygen bond in phenols has a partial double bond character and is difficult to break being stronger than a single bond.

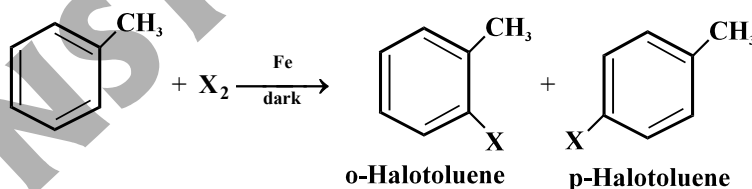
Q. Identify all the possible monochloro structural isomers expected to be formed on free radical monochlorination of $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$. [NCERT Solved Example 10.3]

Solution : In the given molecule, there are four different types of hydrogen atoms. Replacement of these hydrogen atoms will give the following



Q. How the o-Halotoluene and p-Halotoluene is prepared from toluene ?

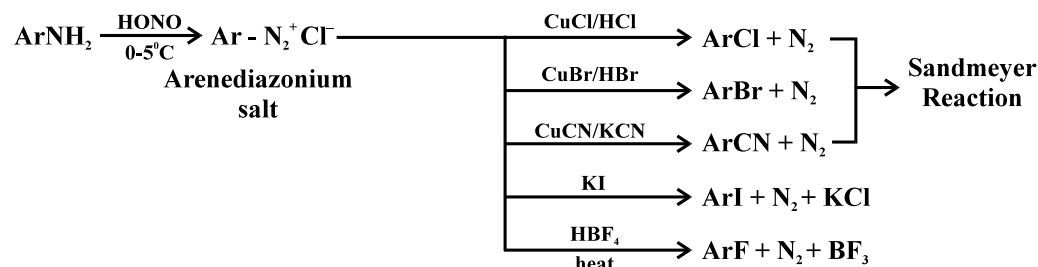
Solution : Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts like iron or iron(III) chloride.



The ortho and para isomers can be easily separated due to large difference in their melting points. Reactions with iodine are reversible in nature and require the presence of an oxidising agent (HNO_3 , HIO_4) to oxidise the HI formed during iodination. Fluoro compounds are not prepared by this method due to high reactivity of fluorine.

Q. Explain the formation of aryl halide from aniline.

Solution :

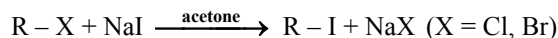


Iodine is not easily introduced into the benzene ring directly, but, when the diazonium salt solution is treated with potassium iodide, iodobenzene is formed.

When arenediazonium chloride is treated with fluoroboric acid, arene diazonium fluoroborate is precipitated which on heating decomposes to yield aryl fluoride.

Q. Explain the Finkelstein and Swarts reaction.

Solution : Halide exchange (Finkelstein reaction)



An alkyl iodide is prepared often from the corresponding bromide or chloride by treatment with a solution of sodium iodide in acetone; the less soluble bromide or sodium chloride precipitate from the solution and can be removed by filtration.

Swarts Reaction : $CH_3Br + AgF \rightarrow CH_3F + AgBr$

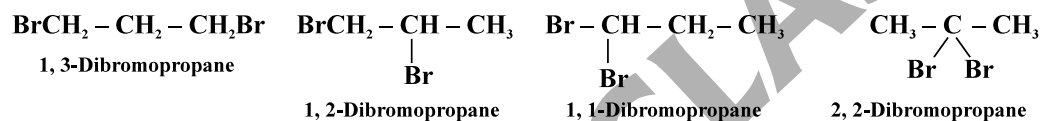
It is the best way to prepare alkyl fluorides by halogen exchange by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as AgF , Hg_2F , CoF_2 or SbF_3 .

Q. Why is sulphuric acid not used during the reaction of alcohols with KI ?

Solution : It oxidises HI produced during the reaction to I_2

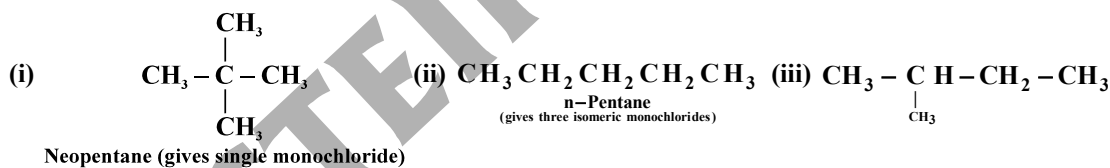
Q. Write structures of different dihalogen derivatives of propane.

Solution :

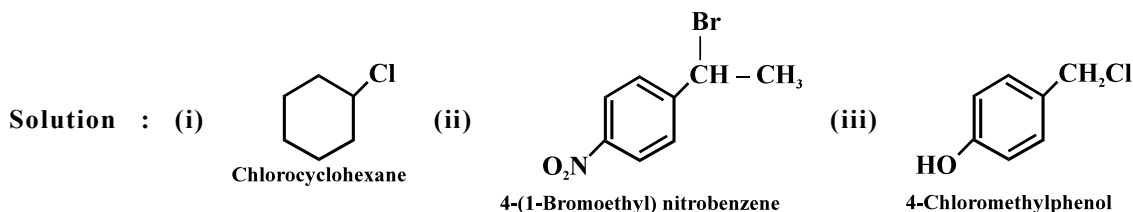
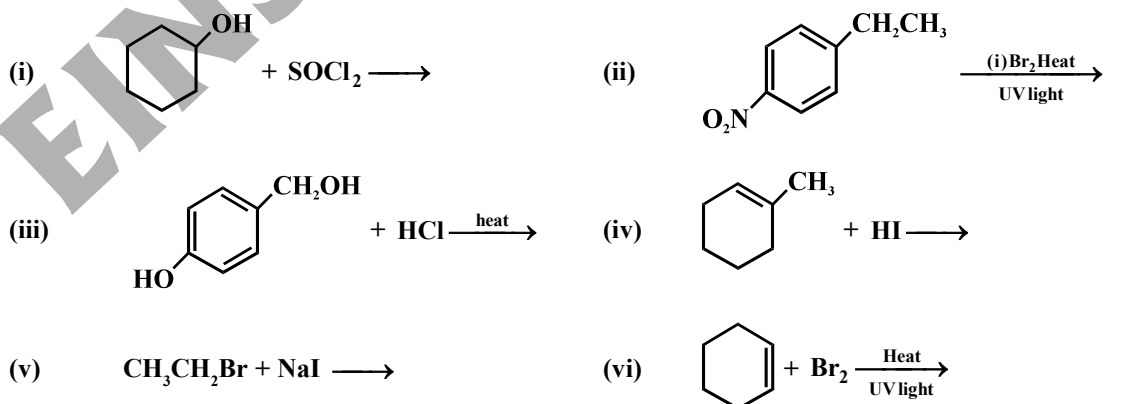


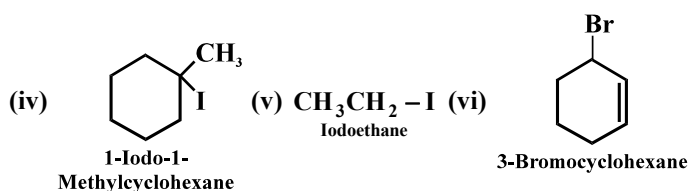
Q. Among the isomeric alkanes of molecular formula C_5H_{12} , identify the one that on photochemical chlorination yields (i) a single monochloride (ii) three isomeric monochlorides (iii) four isomeric monochlorides.

Solution :



Q. Draw the structures of major monohalo products in each of the following reactions :





10.5 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.

Q. Boiling point of Alkyl halide is greater than hydrocarbon. Explain it.

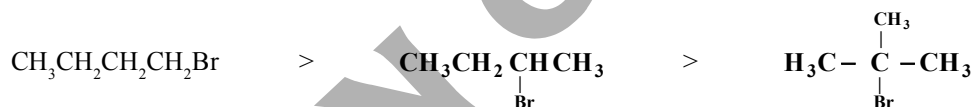
Solution : Molecules of organic halogen compounds are generally polar. Due to greater polarity as well as higher molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction (dipole-dipole and van der Waals) are stronger in the halogen derivatives. That is why the boiling point of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons of comparable molecular mass.

Q. Arrange the RI, RF, RCl, RBr in the decreasing order of boiling point.

Solution : The attractions get stronger as the molecules get bigger in size and have more electrons. The pattern of variation of boiling points of different halides is depicted. For the same alkyl group, the boiling point of alkyl halides decrease in the order : $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$. This is because with the increase in size and mass of halogen atom, the magnitude of van der Waal forces increases.

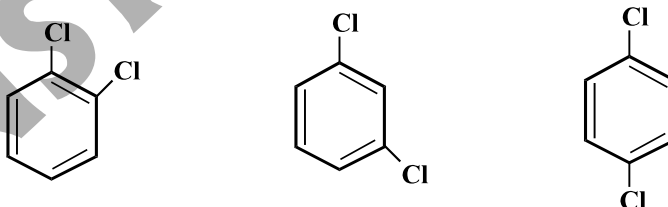
Q. What is the effect of branching on the boiling point of haloalkanes ?

Solution : The boiling points of isomeric haloalkanes decrease with increase in branching. For example, 2-bromo-2-methylpropane has the lowest boiling point among the three isomers.



Q. Explain the boiling point and melting point of ortho, meta, para di-chloro benzene.

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



Q. Whether the density of alkyl halide is more or less than the water.

Solution : Bromo, iodo and polychloro derivatives of hydrocarbons are heavier than water. The density increases with increase in number of carbon atoms, halogen atoms and atomic mass of the halogen atoms.

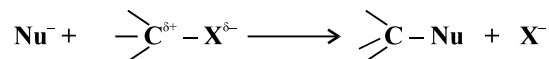
Q. Why solubility of haloalkanes in water is low ?

Solution : The haloalkanes are only very slightly soluble in water. In order for a haloalkane to dissolve in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules. Less energy is released when new attractions are set up between the haloalkanes and the water molecules as these are not as strong as the original hydrogen bonds in water. As a result, the solubility of haloalkanes in water is low. However, haloalkanes tend to dissolve in organic solvents because the new intermolecular attractions between haloalkanes and solvent molecules have much the same strength as the ones being broken in the separate haloalkane and solvent molecules.

10.6 Chemical Reactions :

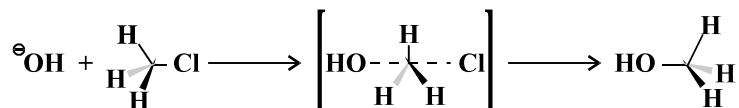
Q. Explain the nucleophilic substitution reaction of alkyl halide.

Solution : In this type of reaction, a nucleophile reacts with haloalkane (the substrate) 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.

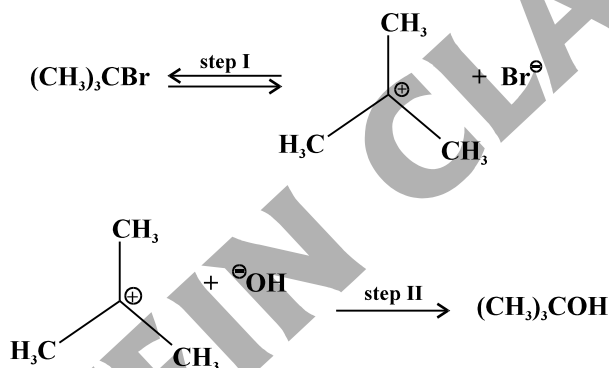


Substitution nucleophilic bimolecular (S_N2) :

The reaction between CH_3Cl and hydroxide ion to yield methanol and chloride ion follows a second order kinetics, i.e., the rate depends upon the concentration of both the reactants.



Substitution nucleophilic unimolecular (S_N1) :



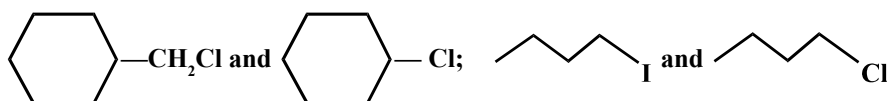
Q. Write the difference between S_N1 and S_N2 mechanism.

Solution :


S_{N1}	S_{N2}
1. Rate law expression is $r = k[\text{RX}]$	Rate law expression is $r = k[\text{RX}][\text{Z}^-]$
2. First order reaction	Second order reaction
3. Intermediate is carbocation	Transition state is formed
4. Order of reactivity of RX $3^\circ > 2^\circ > 1^\circ > \text{CH}_3\text{X}$	Order of reaction of RX $\text{CH}_3\text{X} > 1^\circ > 2^\circ > 3^\circ$
5. $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$	$\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$

Q. In the following pairs of halogen compounds, which would undergo S_N2 reaction faster ? [NCERT

Solved Example 10.6]



Solution : $\text{Cyclohexane ring}-\text{CH}_2\text{Cl}$: It is a primary halide and therefore undergoes S_N2 reaction faster.

 : As iodine is a better leaving group because of its large size, it will be released at a faster rate in the presence of incoming nucleophile.

Q. Predict the order of reactivity of the following compounds in S_{N1} and S_{N2} reactions : (i) The four isomeric bromobutanes (ii) $C_6H_5CH_2Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$, $C_6H_5C(CH_3)(C_6H_5)Br$ [NCERT Solved Example 10.7]

Solution : (i) $CH_3CH_2CH_2CH_2Br < (CH_3)_2CHCH_2Br < CH_3CH_2CH(Br)CH_3 < (CH_3)_3CBr$ (S_{N1})

$CH_3CH_2CH_2CH_2Br > (CH_3)_2CHCH_2Br > CH_3CH_2CH(Br)CH_3 > (CH_3)_3CBr$ (S_{N2})

(ii) $C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$ (S_{N1})

$C_6H_5C(CH_3)(C_6H_5)Br < C_6H_5CH(C_6H_5)Br < C_6H_5CH(CH_3)Br < C_6H_5CH_2Br$ (S_{N2})

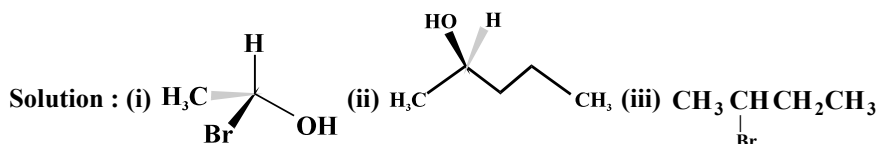
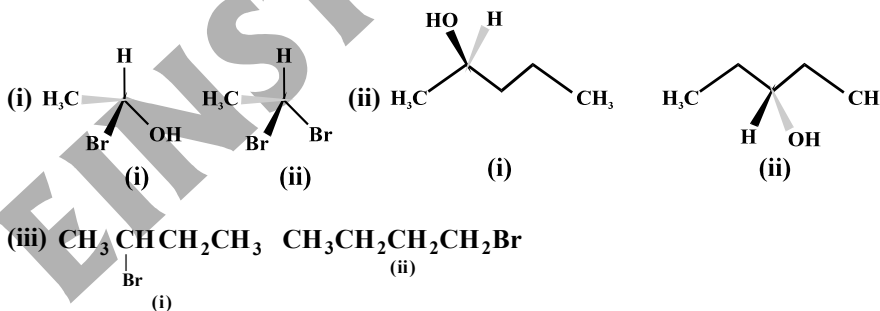
Q. What are optical isomer and what is the cause of optical activity of a molecule ?

Solution : The compounds having similar physical and chemical properties but differing only in the behaviour towards the plane polarised light are called as optical isomers.

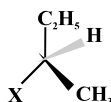
On the basis of study of optical activity, the various organic compounds are divided into three types : (a) The optical isomer with rotate the plane of polarised light to the right are called as dextrorotatory or d-form or indicated by + sign. (b) The optical isomer which rotate the plane of polarised light to the left are called as levorotatory or l-form on indicated by -ve sign. (c) The optical powers of the above two isomers are same i.e. of same magnitude but of opposite sign. (d) The equimolar mixture of two forms, therefore will be optically inactive. This mixture is termed is **Racemic Mixture**.

Cause of Optical Activity or Optical Isomerism : A plane which divides an object into two symmetrical halves is said to have a plane of symmetry. An object lacking a plane of symmetry is called **dissymmetric or chiral**. A symmetric object is called as **achiral**. A dissymmetrical or chiral object can be defined as the one which is not super imposable on its mirror image. In order to exhibit optical activity an object must be chiral. The compounds which are mirror images of each other but not super imposable are called as **enantiomers**. Generally compounds having carbon atom to which four different groups are when attached show optical isomerism.

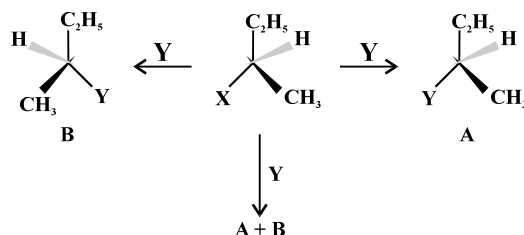
Q. Identify chiral and achiral molecules in each of the following pair of compounds. (Wedge and Dash representations according to Class XI)



Q. Explain the inversion, retention and racemisation in the following compounds if X is replaced by Y.



Solution :



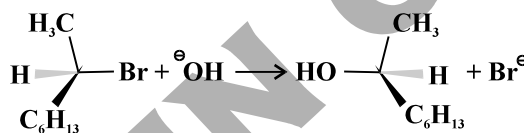
If (A) is the only compound obtained, the process is called retention of configuration. Retention of configuration is the preservation of integrity of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction or transformation.

If (B) is the only compound obtained, the process is called inversion of configuration.

If a 50:50 mixture of the above two is obtained then the process is called racemisation and the product is optically inactive, as one isomer will rotate light in the direction opposite to another.

Q. In S_N2 reaction of optically active halides complete inversion of configuration takes place. Explain it.

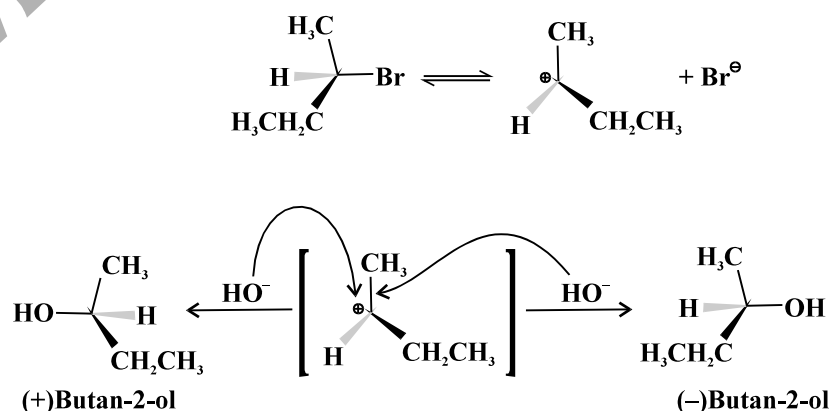
Solution : In case of optically active alkyl halides, the product formed as a result of S_N2 mechanism has the inverted configuration as compared to the reactant. This is because the nucleophile attaches itself on the side opposite to the one where the halogen atom is present. When (–)-2-bromooctane is allowed to react with sodium hydroxide, (+)-octan-2-ol is formed with the –OH group occupying the position opposite to what bromide had occupied.



Thus, S_N2 reactions of optically active halides are accompanied by inversion of configuration.

Q. S_N1 reaction are accompanied by racemisation. Explain it.

Solution : In S_N1 reaction the carbocation formed in the slow step being sp^2 hybridised is planar (achiral). The attack of the nucleophile may be accomplished from either side resulting in a mixture of products, one having the same configuration (the –OH attaching on the same position as halide ion) and the other having opposite configuration (the –OH attaching on the side opposite to halide ion). This may be illustrated by hydrolysis of optically active 2-bromobutane, which results in the formation of (+)-butan-2-ol.



Q. Give the example of S_N2 reaction of alkyl halide.

Solution : (i) Formation of alcohol from alkyl halide (a) $R : X + ^-OH \longrightarrow ROH + :X^-$

(b) $R : X + H_2O \longrightarrow ROH$

(ii) Formation of ether from alkyl halide : $R : X + ^-O R' \longrightarrow ROR'$ (Williamson's Synthesis)

(iii) Formation of alkyne from alkyl halide : $RX + ^-C \equiv C R' \longrightarrow R - C \equiv CR$

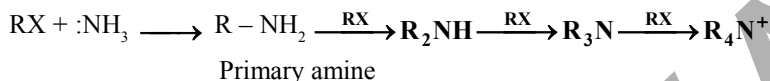
(iv) Formation of alkane from alkyl halide : $RX + \delta^- R' - M^{\delta+} \longrightarrow R - R'$

(v) Formation of cyanide from alkyl halide : $\underset{\text{alkyl halide}}{RX} + KCN \longrightarrow \underset{\text{alkyl cyanide}}{RCN} + KX$

(vi) Formation of isocyanide from alkyl halide : $\underset{\text{alkyl halide}}{RX} + AgCN \longrightarrow \underset{\text{alkyl isocyanide}}{RNC} + AgX$

(vii) Formation of ester : $RX + R' COOAg \longrightarrow R'COOR + AgX$

(viii) Formation of ammonolysis :

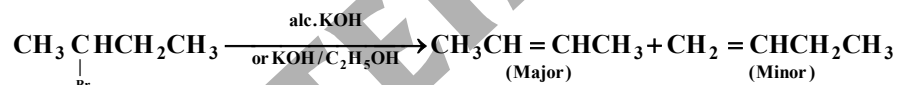


(ix) Formation of nitrocompound from alkyl halide : $\underset{\text{alkyl halide}}{RX} + AgNO_2 \longrightarrow \underset{\text{nitro alkane}}{RNO_2} + AgX$

(x) Formation of nitrite from alkyl halide : $\underset{\text{alkyl halide}}{RX} + KNO_2 \longrightarrow \underset{\text{alkyl nitrite}}{RONO} + AgX$

Q. Explain the dehydrohalogenation reaction of alkyl halide.

Solution : Dehydrohalogenation reaction is also known as elimination reaction.

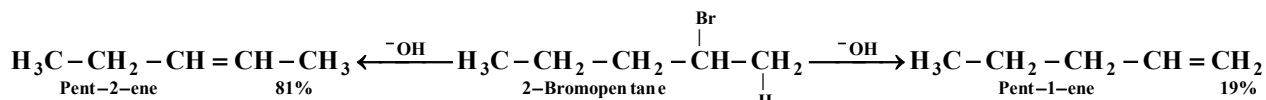


Elimination mechanism is possible in two ways i.e., E_1 and E_2 :

E_1	E_2
1. Rate law expression is $r = k[RX]$	Rate law expression is $r = k[RX][B^-]$
2. First order reaction	Second order reaction
3. Intermediate is carbocation	Transition state is formed
4. Order of reactivity of RX $3^\circ > 2^\circ > 1^\circ$	Order of reaction of RX $3^\circ > 2^\circ > 1^\circ$
5. $RI > RBr > RCl > RF$	$RI > RBr > RCl > RF$

Q. Define the Saytzeff rule.

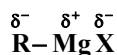
Solution : Alexander Zaitsev (also pronounced as Saytzeff) who in 1875 formulated a rule which can be summarised as "in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms. Thus, 2-bromopentane gives pent-2-ene as the major product.



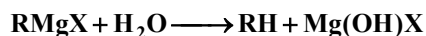
Q. Explain the formation of Grignard Reagent.

Solution : Preparation of Grignard reagent : $R - X + Mg \xrightarrow{\text{ether}} R - MgX$

In the Grignard reagent, the carbon-magnesium bond is covalent but highly polar, with carbon pulling electrons from electropositive magnesium; the magnesium halogen bond is essentially ionic.



Grignard reagents are highly reactive and react with any source proton to give hydrocarbons. Even water, alcohols, amines are sufficiently acidic to convert them to corresponding hydrocarbons.

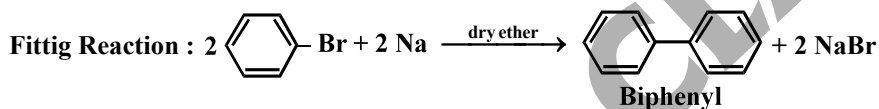
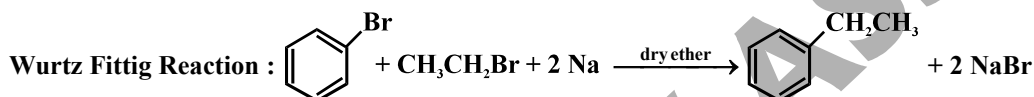


It is therefore necessary to avoid even traces of moisture from a Grignard reagent. On the other hand, this could be considered as one of the methods for converting halides to hydrocarbons.

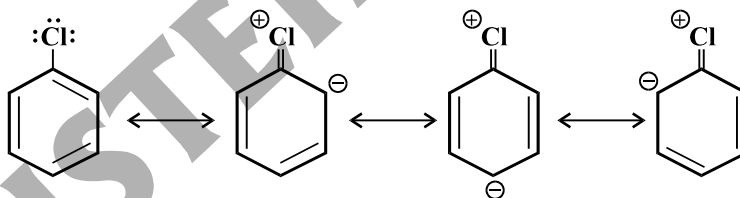
Q. Explain the Wurtz reaction, Wurtz-Fittig reaction and Fittig reaction.

Solution : Wurtz Reaction : $2R - X \xrightarrow{Na/dry\ ether} R - R + NaX.$

(both molecules of alkyl halides can be used different)

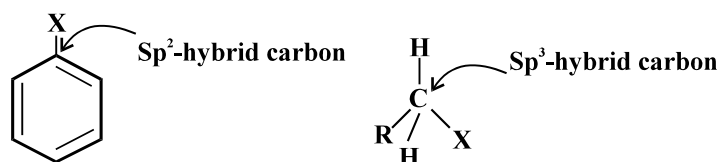
**Q. Why aryl halides are extremely less reactive towards nucleophilic substitution reaction ?**

Solution : (i) Resonance effect : In haloarenes, the electron pairs on halogen atom are in conjugation with π -electrons of the ring and the following resonating structures are possible.



C — Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarenes is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

(ii) Difference in hybridisation of carbon atom in C—X bond : In haloalkane, the carbon atom attached to halogen is sp^3 hybridised while in case of haloarene, the carbon atom attached to halogen is sp^2 -hybridised.



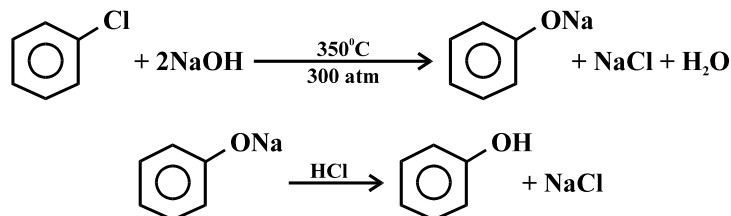
The sp^2 hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of C — X bond more tightly than sp^3 -hybridised carbon in haloalkane with less s-character. Thus, C—Cl bond length in haloalkane is 177pm while in haloarene is 169 pm. Since it is difficult to break a shorter bond than a longer bond, therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

(iii) Instability of phenyl cation : In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore, S_N1 mechanism is ruled out.

(iv) Because of the possible repulsion, it is less likely for the electron rich nucleophilic to approach electron rich arenes.

Q. How the phenol is formed from chlorobenzene ?

Solution : Hydrolysis of Chlorobenzene (Dow Process) :

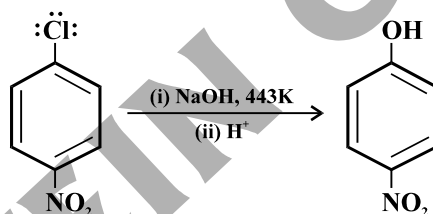


Q. Can you think why the NO₂ group show its effect only at ortho- and para- positions and not at meta- position in Aryl halide ?

Solution : 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 -NO₂ group while in case of meta-nitrobenzene, none of the resonating structures bear the negative charge on carbon atom bearing the -NO₂ group. Therefore, the presence of nitro group at meta- position does not stabilise the negative charge and no effect on reactivity is observed by the presence of -NO₂ group at meta-position.

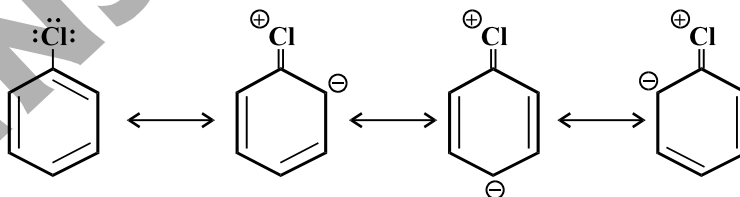
Q. Convert p-nitro chlorobenzene to p-nitro phenol.

Solution : The presence of an electron withdrawing group (-NO₂) at ortho- and para-positions increases the reactivity of haloarenes.



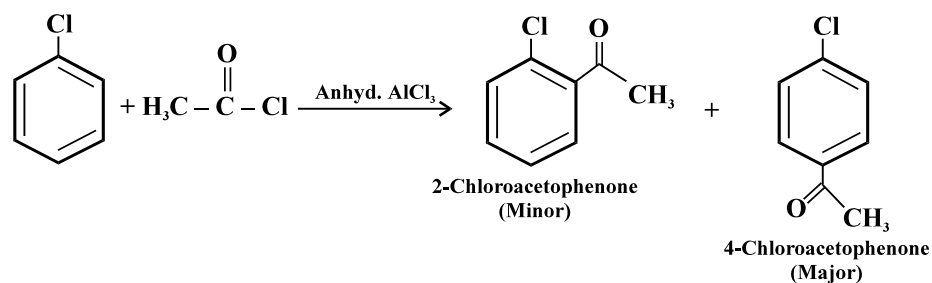
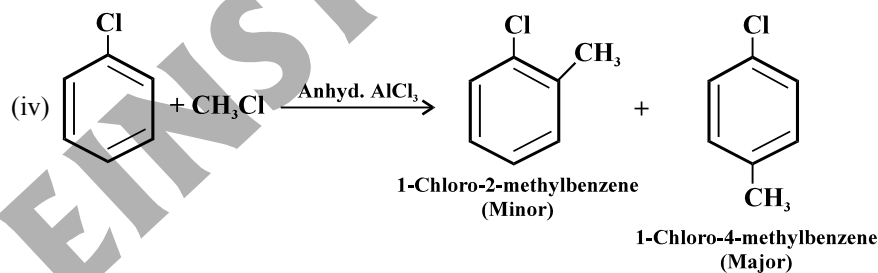
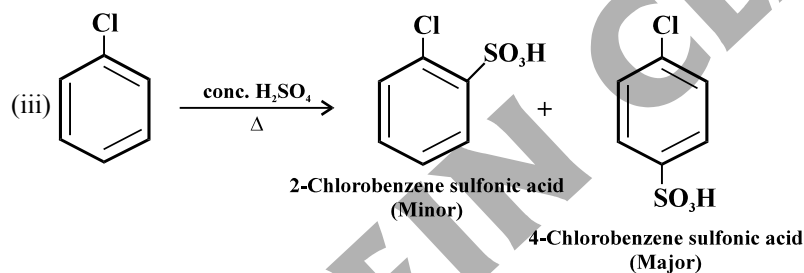
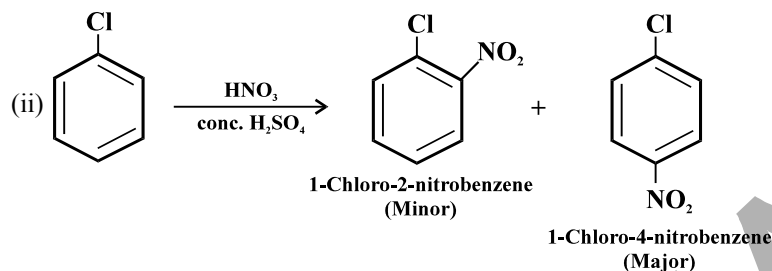
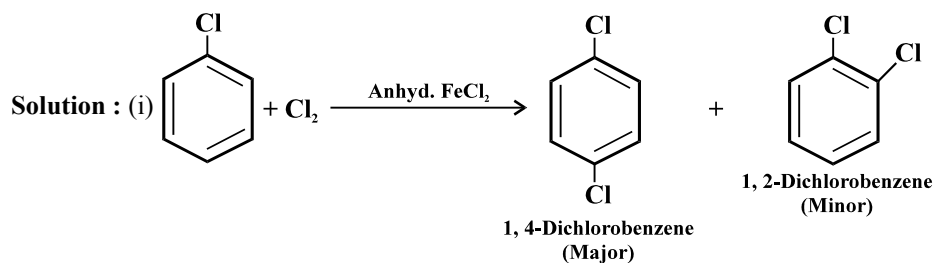
Q. Why haloarenes shows ortho- and para- directing effect in electrophilic substitution reaction ? Also explain why they are weakly deactivating in nature.

Solution :



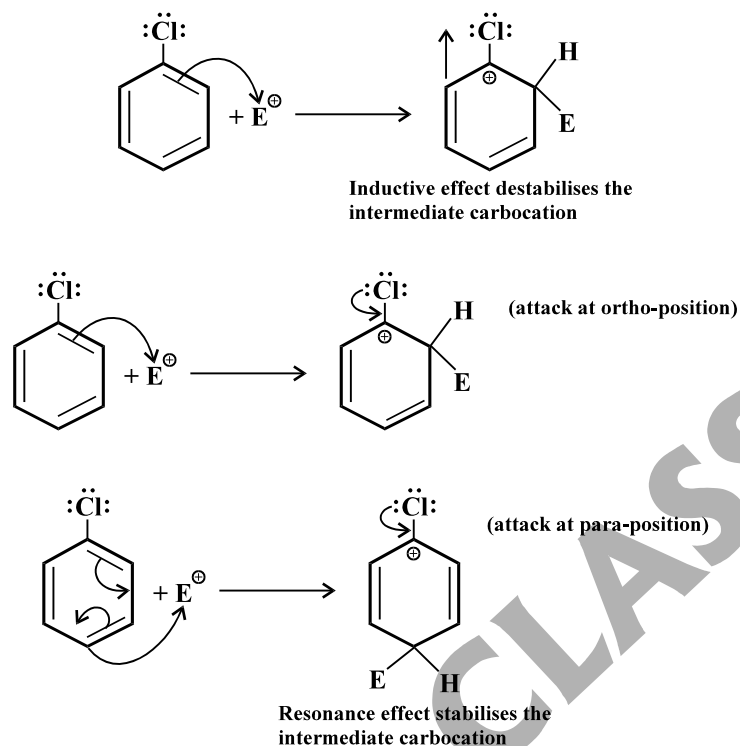
Due to resonance, the electron density increases more at ortho- and para-positions than at meta-positions. Further, the halogen atom because of its -I effect has some tendency to withdraw electrons from the benzene ring. As a result, the ring gets somewhat deactivated as compared to benzene and hence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

Q. Write a note on following reaction : (i) Halogenation of Chlorobenzene (ii) Nitration of Chlorobenzene (iii) Sulfonation of Chlorobenzene (iv) Fredel Craft Alkylation and Acetylation of Chlorobenzene.



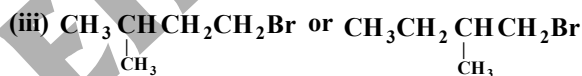
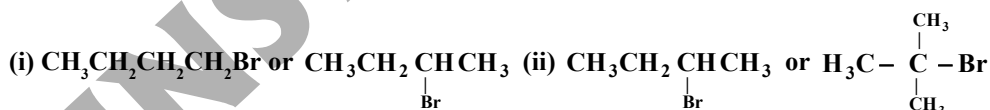
Q. Although chlorine is an electron withdrawing group, yet it is ortho-, para- directing in electrophilic aromatic substitution reactions. Why ? [NCERT Solved Example 10.9].

Solution : Chlorine withdraws electrons through inductive effect and releases electrons through resonance. Through inductive effect, chlorine destabilises the intermediate carbocation formed during the electrophilic substitution.

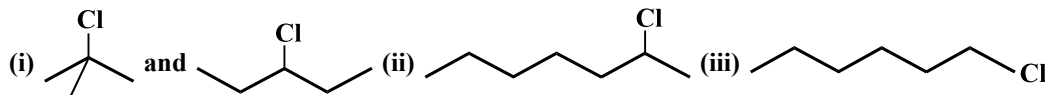


Through resonance, halogen tends to stabilise the carbocation and the effect is more pronounced at ortho- and para- positions. The inductive effect is stronger than resonance and causes net electron withdrawal and thus causes net deactivation. The resonance effect tends to oppose the inductive effect 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.

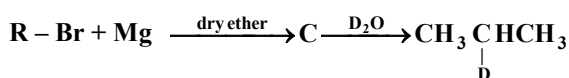
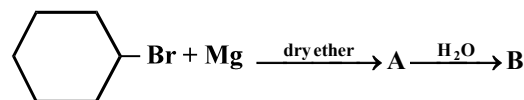
Q. Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism ? Explain your answer.

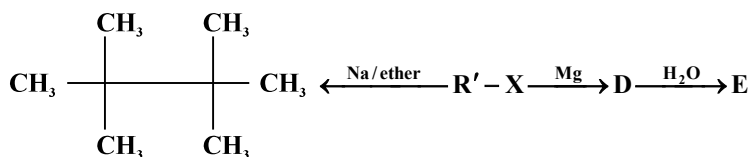


Q. In the following pairs of halogen compounds, which component undergoes faster S_N1 reaction ?



Q. Identify A, B, C, D, E, R and R¹ in the following :





10.7 Polyhalogen Compounds :

Q. Write a note on methylene chloride, chloroform, iodoform, carbon tetrachloride, freons and DDT.

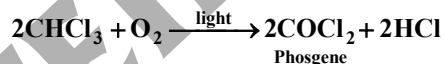
Solution : Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds. Many of these compounds are useful in industry and agriculture. Some polyhalogen compounds are described in this section.

Dichloromethane (Methylene chloride) :

Dichloromethane is widely used as a solvent as a paint remover, as 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. 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 of methylene chloride in air 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.

Trichloromethane (Chloroform) :

Chemically, chloroform is employed as a solvent for fats, alkaloids, iodine and other substances. The major use of chloroform today is in the production of the freon refrigerant R-22. It was once used as a general anaesthetic in surgery but has been replaced by less toxic, safer anaesthetics, inhaling chloroform vapours depresses the central nervous system. Breathing about 900 parts of chloroform per million parts of air (900 parts per million) for a short time can cause dizziness, fatigue, and headache. Chronic chloroform exposure may cause damage to the liver (where chloroform is metabolised to phosgene) and to the kidneys, and some people develop sores when the skin is immersed in chloroform. Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as phosgene. It is therefore stored in closed dark coloured bottles completely filled so that air is kept out.



Triiodomethane (Iodoform) :

It was used earlier as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to iodoform itself. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

Tetrachloromethane (Carbon tetrachloride) :

It is produced in large quantities for use in the manufacture of refrigerants and propellants for aerosol cans. It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, pharmaceutical manufacturing, and general solvent use. Until the mid 1960s, it was also widely used as a cleaning fluid, both in industry, as a degreasing agent, and in the home, as a spot remover and as fire extinguisher. There is some evidence that exposure to carbon tetrachloride causes liver cancer in humans. The most common effects are dizziness, light headedness, nausea and vomiting, which can cause permanent damage to nerve cells. In severe cases, these effects can lead rapidly to stupor, coma, unconsciousness or death. Exposure to CCl_4 can make the heart beat irregularly or stop. The chemical may irritate the eyes on contact. When carbon tetrachloride is released into the air, it rises to the atmosphere and depletes the ozone layer. Depletion of the ozone layer is believed to increase human exposure to ultraviolet rays, leading to increased skin cancer, eye diseases and disorders, and possible disruption of the immune system.

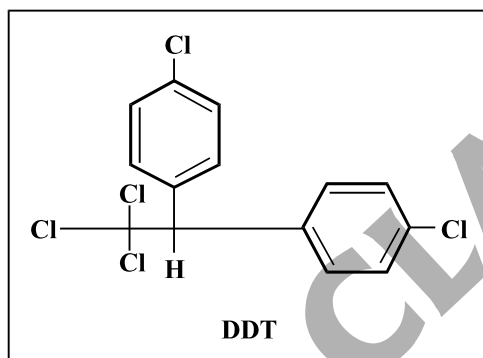
Freons :

The chlorofluorocarbon compounds of methane and ethane are collectively known as feons. They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases. Froen 12 (CCl_2F_2) is one of the most common freons in industrial use. It is manufactured from tetrachloromethane by Swarts reaction. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes. Most freon, even that used in refrigeration, eventually makes its way into the atmosphere where it diffuses

unchanged into the stratosphere. In stratosphere, freon is able to initiate radical chain reactions that can upset the natural ozone balance.

p,p'-Dichlorodiphenyltrichloro ethane (DDT) :

DDT, the first chlorinated organic insecticides, was originally prepared in 1873, but it was not until 1939 that Paul Muller of Geigy Pharmaceuticals in Switzerland discovered the effectiveness of DDT as an insecticide. Paul Muller was awarded the Nobel Prize in Medicine and Physiology in 1948 for this discovery. The use of DDT increased enormously on a worldwide basis after World War II, primarily because of its effectiveness against the mosquito that spreads malaria and lice that carry typhus. However, problems related to extensive use of DDT began to appear in the late 1940s. Many species of insects developed resistance to DDT, and it was also discovered to have a high toxicity towards fish. The chemical stability of DDT and its fat solubility compounded the problem. DDT is not metabolised very rapidly by animals; instead, it is deposited and stored in the fatty tissues. If ingestion continues at a steady rate, DDT builds up within the animal over time. The use of DDT was banned in the United States in 1973, although it is still in use in some other parts of the world.

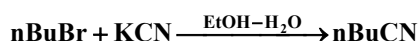


NCERT EXERCISE

- 10.1** Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyly or aryl halides :
- | | |
|--|---|
| (i) $(\text{CH}_3)_2\text{CHCH}(\text{Cl})\text{CH}_3$ | (ii) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{C}_2\text{H}_5)\text{Cl}$ |
| (iii) $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{I}$ | (iv) $(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{Br})\text{C}_6\text{H}_5$ |
| (v) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{Br})\text{CH}_3$ | (vi) $\text{CH}_3\text{C}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{Br}$ |
| (vii) $\text{CH}_3\text{C}(\text{Cl})(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_3$ | (viii) $\text{CH}_3\text{CH}=\text{C}(\text{Cl})\text{CH}_2\text{CH}(\text{CH}_3)_2$ |
| (ix) $\text{CH}_3\text{CH}=\text{CHC}(\text{Br})(\text{CH}_3)_2$ | (x) $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{CH}(\text{CH}_3)_2$ |
| (xi) $m\text{-ClCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}(\text{CH}_3)_3$ | (xii) $o\text{-Br-C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ |
- 10.2** Give the IUPAC names of the following compounds :
- | | |
|--|---|
| (i) $\text{CH}_3\text{CH}(\text{Cl})\text{CH}(\text{Br})\text{CH}_3$ | (ii) $\text{CHF}_2\text{CBrClF}$ |
| (iii) $\text{ClCH}_2\text{C}\equiv\text{CCH}_2\text{Br}$ | (iv) $(\text{CCl}_3)_3\text{CCl}$ |
| (v) $\text{CH}_3\text{C}(p\text{-ClC}_6\text{H}_4)_2\text{CH}(\text{Br})\text{CH}_3$ | (vi) $(\text{CH}_3)_3\text{CCH}=\text{CHCl}(p\text{-IC}_6\text{H}_4)$ |
- 10.3** Write the structures of the following organic halogen compounds :
- | | |
|---|--------------------------------------|
| (i) 2-Chloro-3-methylpentane | (ii) p-Bromochlorobenzene |
| (iii) 1-Chloro-4-ethylcyclohexane | (iv) 2-(2-Chlorophenyl)-1-iodooctane |
| (v) Perfluorobenzene | (vi) 4-tert-Butyl-3-iodoheptane |
| (vii) 1-Bromo-4-sec-butyl-2-methylbenzene | (viii) 1, 4-Dibromobut-2-ene |
- 10.4** Which one of the following has the highest dipole moment ?
- | | | |
|------------------------------|----------------------|----------------------|
| (i) CH_2Cl_2 | (ii) CHCl_3 | (iii) CCl_4 |
|------------------------------|----------------------|----------------------|
- 10.5** A 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. Identify the hydrocarbon.
- 10.6** Write the isomers of the compound having formula $\text{C}_4\text{H}_9\text{Br}$.
- 10.7** Write the equations for the preparation of 1-iodobutane from
- | | | |
|---------------|---------------------|-----------------|
| (i) 1-butanol | (ii) 1-chlorobutane | (iii) but-1-ene |
|---------------|---------------------|-----------------|
- 10.8** What are ambident nucleophiles ? Explain with an example.
- 10.9** Which compound in each of the following pairs will react faster in $\text{S}_{\text{N}}2$ reaction with OH^- ?
- | | |
|---|--|
| (i) CH_3Br or CH_3I | (ii) $(\text{CH}_3)_3\text{CCl}$ or CH_3Cl |
|---|--|
- 10.10** Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene :
- | | |
|--|------------------------------|
| (i) 1-Bromo-1-methylcyclohexane | (ii) 2-chloro-2-methylbutane |
| (iii) 2, 2, 3-trimethyl-3-Bromopentane | |
- 10.11** How will you bring about the following conversions ?
- | | | | |
|---------------------------------|--------------------------------|---------------------------------|--------------------------------|
| (i) Ethanol to but-1-yne | (ii) Ethane to bromoethene | (iii) Propene to 1-nitropropane | (iv) Toluene to benzyl alcohol |
| (v) Propene to propyne | (vi) Ethanol to ethyl fluoride | (vii) Bromomethane to propanone | (viii) But-1-ene to but-2-ene |
| (ix) 1-Chlorobutane to n-octane | (x) Benzene to biphenyl. | | |
- 10.12** Explain, why
- | |
|--|
| (i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride ? |
| (ii) alkyl halides, though polar, are immiscible with water ? |
| (iii) Grignard reagents should be prepared under anhydrous conditions ? |
- 10.13** Give the uses of freon 12, DDT, carbon tetrachloride and iodoform.
- 10.14** Write the structure of the major organic product in each of the following reactions :
- | |
|---|
| (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{NaI} \xrightarrow[\text{heat}]{\text{acetone}}$ |
|---|

- (ii) $(\text{CH}_3)_3\text{CBr} + \text{KOH} \xrightarrow[\text{heat}]{\text{ethanol}}$
- (iii) $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3 + \text{NaOH} \xrightarrow{\text{water}}$
- (iv) $\text{CH}_3\text{CH}_2\text{Br} + \text{KCN} \xrightarrow{\text{aq. ethanol}}$
- (v) $\text{C}_6\text{H}_5\text{ONa} + \text{C}_2\text{H}_5\text{Cl} \longrightarrow$
- (vi) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{SOCl}_2 \longrightarrow$
- (vii) $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{HBr} \xrightarrow{\text{peroxide}}$
- (viii) $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2 + \text{HBr} \longrightarrow$

10.15 Write the mechanism of the following reaction :



10.16 Arrange the compounds of each set in order of reactivity towards $\text{S}_{\text{N}}2$ displacement :

- (i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane
- (ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane
- (iii) 1-Bromobutane, 1-Bromo-2, 2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.

10.17 Out of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ and $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$ which is more easily hydrolysed by aqueous KOH ?

10.18 p-Dichlorobenzene has higher m.p. and solubility than those of o- and m-isomers. Discuss.

10.19 How the following conversions can be carried out ?

- | | |
|--|--|
| (i) Propene to propan-1-ol | (ii) Ethanol to but-1-yne |
| (iii) 1-Bromopropane to 2-bromopropane | (iv) Toluene to benzyl alcohol |
| (v) Benzene to 4-bromonitrobenzene | (vi) Benzyl alcohol to 2-phenylethanoic acid |
| (vii) Ethanol to propanenitrile | (viii) Aniline to chlorobenzene |
| (ix) 2-Chlorobutane to 3, 4-dimethylhexane | (x) 2-methyl-1-propene to 2-chloro-2-methylpropane |
| (xi) Ethyl chloride to propanoic acid | (xii) But-1-ene to n-butyliodide |
| (xiii) 2-chloropropane to 1-propanol | (xiv) Isopropyl alcohol to iodoform |
| (xv) Chlorobenzene to p-nitrophenol | (xvi) 2-Bromopropane to 1-bromopropane |
| (xvii) Chloroethane to butane | (xviii) Benzene to diphenyl |
| (xix) tert-Butyl bromide to isobutyl bromide | (xx) Aniline to phenylisocyanide |

10.20 The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major product. Explain.

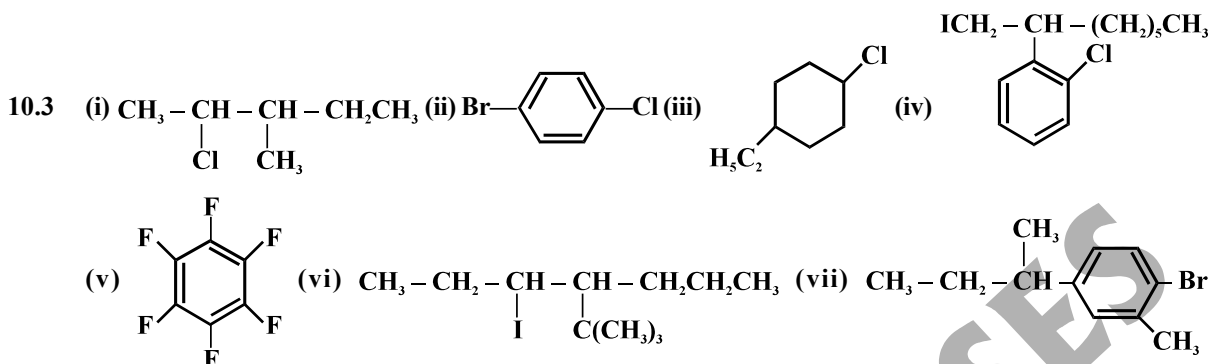
10.21 Primary alkyl halide $\text{C}_4\text{H}_9\text{Br}$ (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

10.22 What happens when

- (i) n-butyl chloride is treated with alcoholic KOH.
- (ii) bromobenzene is treated with Mg in the presence of dry ether.
- (iii) chlorobenzene is subjected to hydrolysis.
- (iv) ethyl chloride is treated with aqueous KOH.
- (v) methyl bromide is treated with sodium in the presence of dry ether.
- (vi) methyl chloride is treated with KCN ?

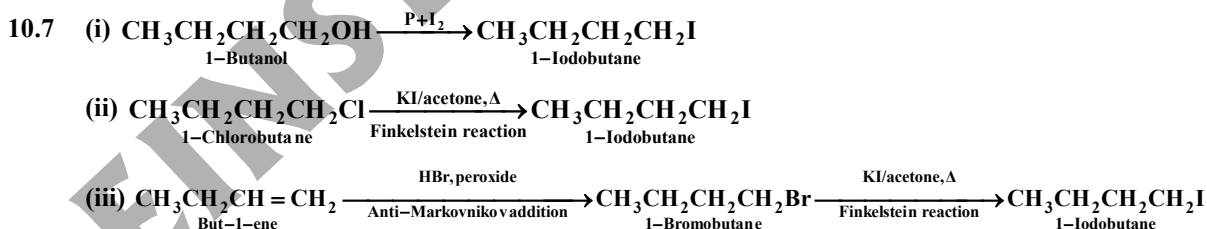
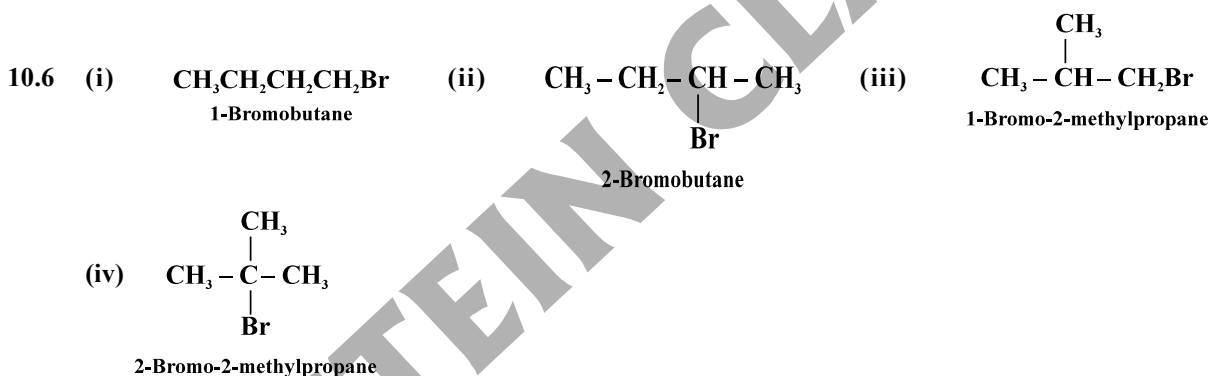
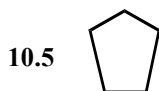
ANSWERS

- 10.2 (i) 2-Bromo-3-chlorobutane (ii) 1-Bromo-1-chloro-1, 2, 2-trifluoroethane, (iii) 1-Bromo-4-chlorobut-2-yne (iv) 2-(Trichloromethyl)-1, 1, 1, 2, 3, 3, 3-heptachloropropane (v) 2-Bromo-3, 3-bis(4-chlorophenyl)butane (vi) 1-Chloro-1-(4-iodophenyl)-3, 3-dimethylbut-1-ene.



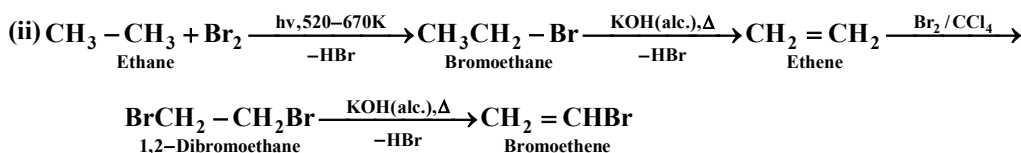
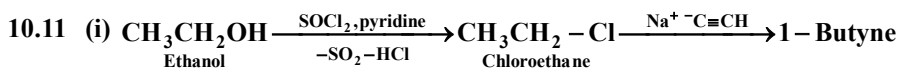
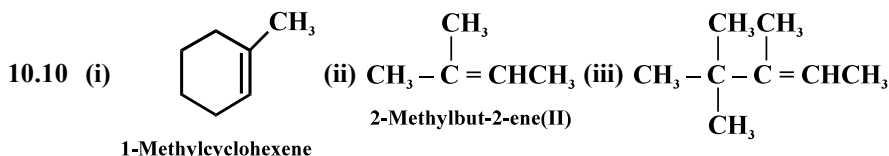
(viii) $\text{BrCH}_2\text{CH} = \text{CHCH}_2\text{Br}$

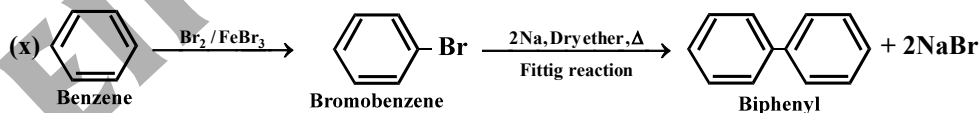
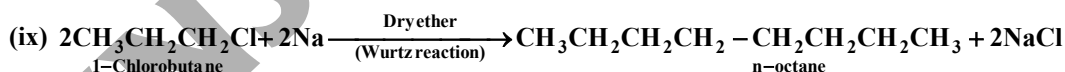
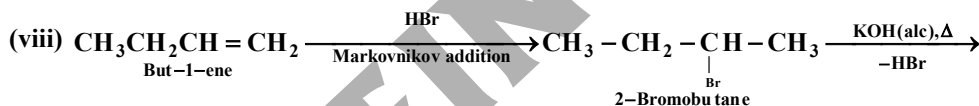
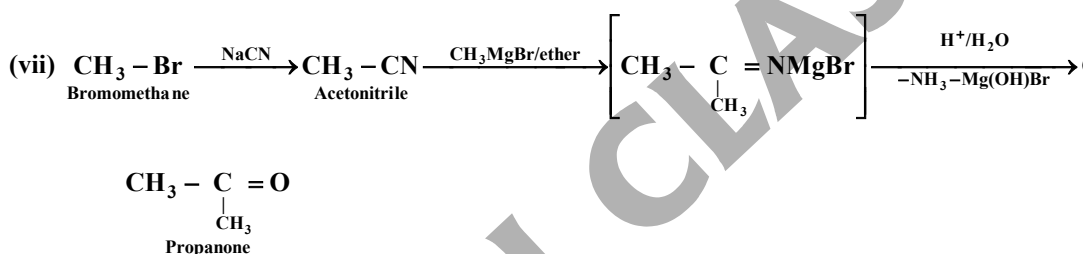
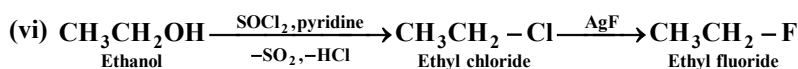
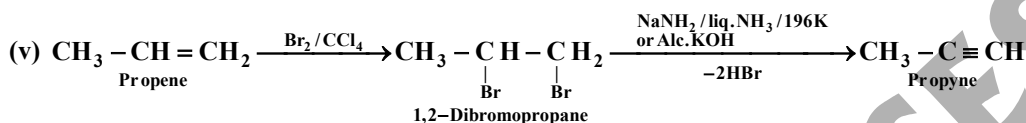
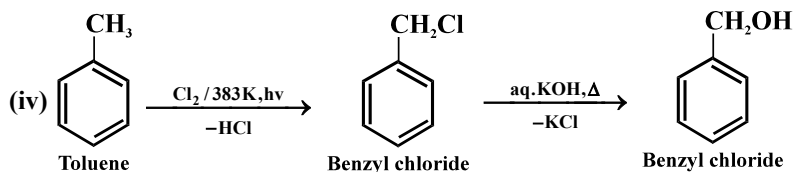
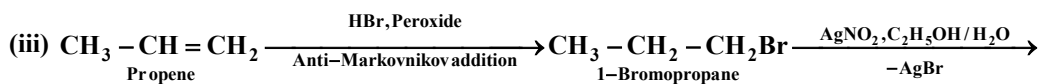
- 10.4 CH_2Cl_2 has the highest dipole moment



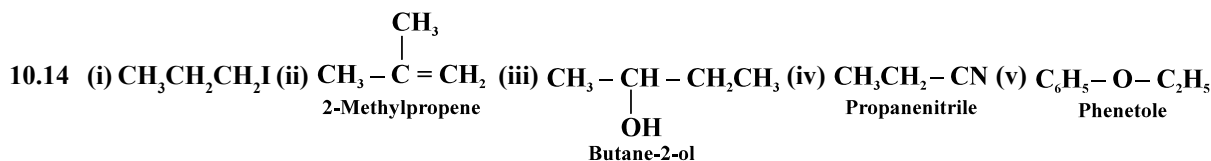
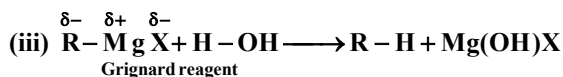
10.8 cyanide ion

- 10.9 (i) CH_3I (ii) CH_3Cl





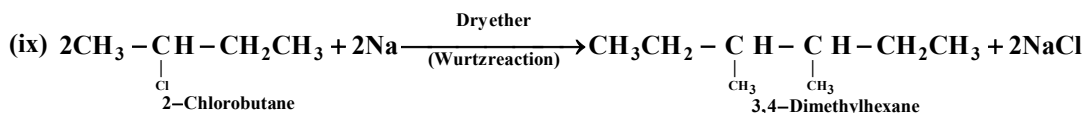
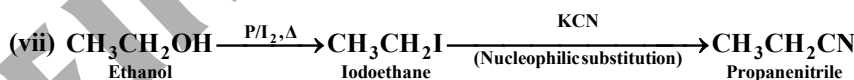
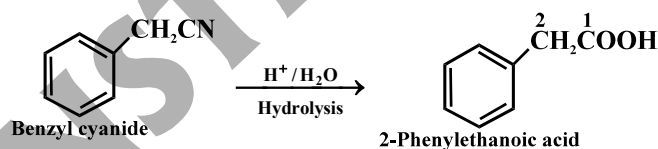
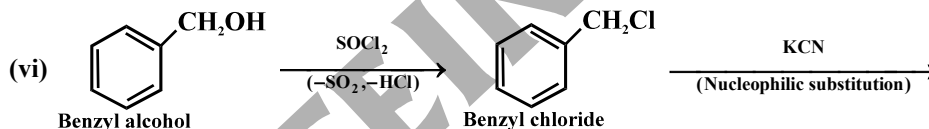
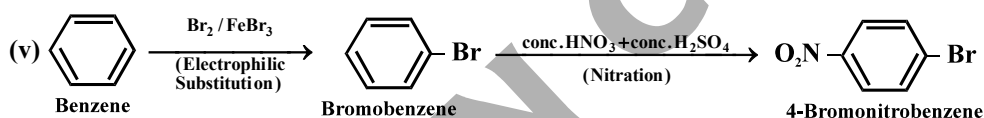
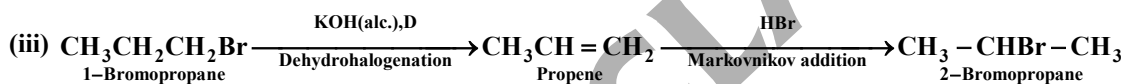
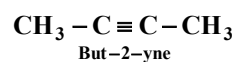
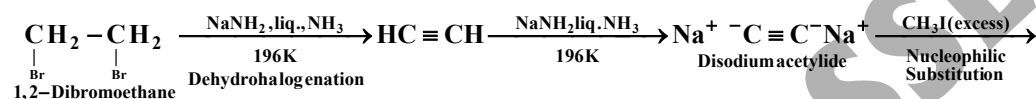
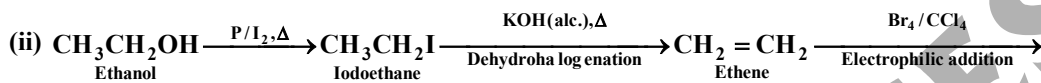
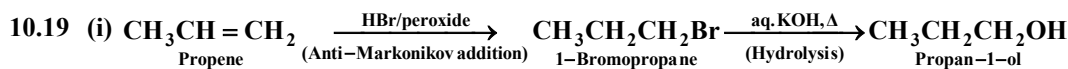
10.12 (i) sp^2 -hybrid carbon is more electronegative than a sp^3 -hybrid carbon (ii) Since the new forces of attraction between water and alkyl halide molecules are weaker than the forces of attraction already existing alkyl halide-alkyl halide molecules and water-water molecules.




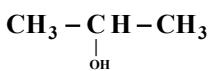


10.16 (i) 1-Bromopentane > 2-Bromopentane > 2-Bromo-2-methylbutane (ii) 1-Bromo-3-methylbutane > 2-Bromo-3-methylbutane > 2-Bromo-2-methylbutane (iii) 1-Bromobutane > 1-Bromo-3-methylbutane > 1-Bromo-2-methylbutane > 1-Bromo-2, 2 dimethylpropane.

10.17 $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$ gets hydrolysed more easily than $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ under $\text{S}_{\text{N}}1$ conditions.



ADDITIONAL QUESTIONS AND PROBLEMS

- Q. (i) Explain the following with the help of suitable examples :
- (a) Carbylamine reaction
 - (b) Finkelstein reaction
- (ii) Give one chemical test to distinguish between ethanol and 1-propanol.
- Q. How will you effect the following two steps conversions ?
- (a) Chlorobenzene to p-nitrophenol
 - (b) Bromobenzene to diphenyl
- Q. Write the structure of main products :
- (i) Chlorination of benzene in presence of U.V. light
 - (ii) Propene is treated with HBr in presence of benzoyl peroxide
 - (iii) Chlorobenzene is treated with NaOH at 623 K and high pressure
- Q. Complete the following :
- (i)  + Cl₂ $\xrightarrow{\text{FeCl}_3}$
 - (ii) CH₃COCH₃ + I₂ + NaOH \longrightarrow
- Q. Complete the following reactions :
- (i) CH₃CH₂OH $\xrightarrow{\text{SOCl}_2}$ 'A' $\xrightarrow{\text{KCN}}$ 'B'
 - (ii)  $\xrightarrow{\text{PCl}_5}$ 'A' $\xrightarrow{\text{AgCN}}$ 'B'
 - (iii) CH₃CH₂Cl $\xrightarrow{\text{AgNO}_2}$ 'A'
 - (iv) (CH₃)₂CHCl + CH \equiv CNa \longrightarrow 'A'
 - (v) CH₃CH₂CH₂Cl + CH₃COOAg \longrightarrow 'A' + 'B'
 - (vi) 2(CH₃)₂CHBr + 2Na $\xrightarrow[\text{Ether}]{\text{Dry}}$
- Q. Write chemical equations and reaction conditions for the conversion of :
- (i) Ethene to ethanol
 - (ii) Propene to 1-propanol
 - (iii) Propene to 2-bromopropane
 - (iv) Propene to 2-propanol
 - (v) Chloroform to ethene
 - (vi) Acetylene to vinyl chloride
- Q. An alkyl chloride (A), on reaction with magnesium in dry ether followed by treatment with ethanol gave 2-methylbutane. Write all the possible structures of (A).
- Q. The nucleophilic substitution of primary alkyl chlorides with sodium acetate is catalysed by sodium iodide. Explain why.
- Q. Explain why
- (a) vinyl chloride is unreactive in nucleophilic substitution reactions ?
 - (b) neo-pentyl bromide undergoes nucleophilic substitution reaction very slowly ?
 - (c) 3-bromocyclohexene is more reactive than 4-bromocyclohexene in hydrolysis with aqueous NaOH ?
 - (d) tert-butyl chloride reacts with aqueous sodium hydroxide by S_N1 mechanism while n-butyl chloride reacts by S_N2 mechanism ?