HALOALKANES AND HALOARENES

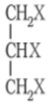
The replacement of one or more hydrogen atoms of a hydrocarbon, aliphatic or aromatic, by an equal number of halogen atom results in the formation of alkyl halide (haloalkanes) and aryl halide (Haloarenes), respectively.

1. Haloalkanes are classified as Fluoro, Chloro, Bromo or Iodo compounds according to the type of halogen present and as mono-, di- tri- haloalkanes, etc., according to the one, two, and three halogen atoms respectively present in their molecule.

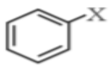
C_2H_5X

Monohaloalkane

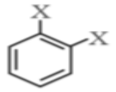
Dihaloalkane



Trihaloalkane

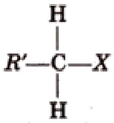


Monohaloarene

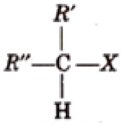


Dihaloarene

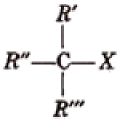
2. Alkyl halides are further classified as primary (1°), secondary (2°) and tertiary (3°) according to the halogen atom attached to primary, secondary and tertiary carbon atoms, respectively. R’CH_2X (Primary), R’R’’CHX (Secondary) and R’R’’R’’’CX (Tertiary)



primary (1°)

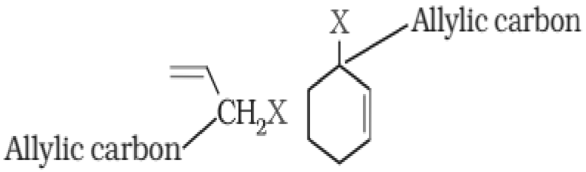


secondary (2°)

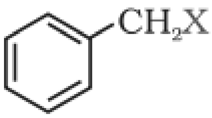


tertiary (3°)

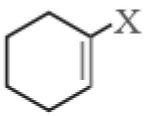
3. Allylic halides:



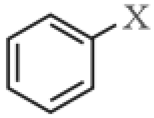
4. Benzylic halides:

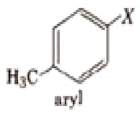


5. Vinylic halides:



6. Aryl halide:





Dihalogen Derivatives: vic-dihalides, gem-dihalides and isolated dihalides.

For examples: vic-dihalides $CH_3 – CH_2 –CH (Cl) – CH_2 Cl$, gem-dihalides $CH_3 – CH_2 –CH (Cl)_2$ isolated dihalides $ClCH_2 – CH_2 -CH_2– CH_2Cl$.

C-X bond is a polar covalent bond due to electronegativity difference between the carbon and the halogen, the shared pair of electron lies closer to the halogen atom. As a result, the halogen carries a small negative charge, while the carbon carries a small positive charge.

Isomerism in Haloalkanes and Haloarenes:

Haloalkanes show two types of isomerism: Chain isomerism and Position isomerism
Haloarenes also show position isomerism.

Methods of Preparation of Haloalkanes:

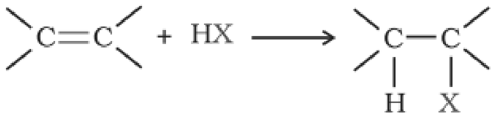
From alcohols: Haloalkanes can be prepared from displacement of alcoholic group in alkyl alcohol by halogen acid, PCl_5 or PCl_3. Haloalkanes can also be prepared by addition of halogen acids or halogens on alkene and alkyne. Alkyl halides can also be prepared by free radical halogenation of alkane.

$R – OH + HCl + ZnCl_2 \rightarrow R - Cl + H_2O$
$R – OH + NaBr + H_2SO_4 \rightarrow R – Br + NaHSO_4 + H_2O$
$R – OH + PX_3 \rightarrow R - X + H_3PO_3$
$R – OH + PCl_5 \rightarrow R - Cl + POCl_3 + HCl$
$R – OH + \xrightarrow{\text{Red P/X2}} R - Cl + H_2O$
$R – OH + SOCl_2 \rightarrow R - Cl + SO_2 + HCl$

Free Radical Halogenation of Alkanes:

$$CH_3CH_2CH_2CH_3 \xrightarrow{\textbf{Cl2}\text{ , UV}} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CH(Cl)\ CH_3$$

Addition of Hydrogen Halides or halogen acids on Alkenes:



During the addition of halogen acids to unsymmetrical alkenes**, Markovnikov rule** is followed, According to this rule during the addition across unsymmetrical double bond, the negative part of the attacking reagent attaches itself to the carbon atom carrying lesser number of hydrogen atoms while the positive part goes to the carbon atom with more number of hydrogen atoms.
Propene + HBr → 2-bromopropane (major product)

Anti-Markovnikov rule or Kharasch effect: In this case of addition of HBr to unsymmetrical alkenes, the negative part of the attacking reagent (Br) will join to the carbon atom carrying more number of hydrogen atoms while H-atom will go to the other carbon atom containing lesser number of hydrogen atoms in the presence of organic peroxide such as benzoyl peroxide ($C_6H_5CO\text{-}O\text{-}O\text{-}COC_6H_5$)
Propene + HBr → 1-bromopropane (major product)

1. Finkelstein Reaction: $R – X + NaI \xrightarrow{\text{Acetone}} R – I + NaX$ (X = Cl, Br)
2. Swarts Reaction: $H_3C – Br + AgF \rightarrow H_3C – F + AgBr$
3. Hunsdiecker Reaction: $CH_3COOAg + Br_2 \xrightarrow{\text{CCl4}} CH_3Br + AgBr + CO_2$

Physical Properties of Haloalkanes:

1. Boiling point orders
    1. $R – I > R – Br > R – Cl > R – F$
    2. $CH_3 – (CH_2)_2 – CH_2Br > (CH_3)_2\ CHCH_2Br > (CH_3)_3CBr$
    3. $CH_3CH_2CH_2X > CH_3CH_2X > CH_3X$

2. Bond enthalpy of haloalkanes decreases as the size of the halogen atom increases. Thus, the order of bond strength is $CH_3F > CH_3Cl > CH_3Br > CH_3I$

3. Dipole moment decreases as the electronegativity of the halogen decreases.

4. Haloalkanes though polar but are insoluble in water as they do not form hydrogen bonding with water.

5. Density: $n\text{-}C_3H_7I > n\text{-}C_3H_7Br > n\text{-}C_3H_7Cl$, $CH_3I > C_2H_5I > C_3H_7I$

5. Chemical reactions of haloalkanes:

KCN is predominantly ionic and provides cyanide ions in solution, which is ambident nucleophile and bind with carbon side to form as the major product, while AgCN is covalent and form isocyanide as the major product.

$CH_3CH_2Br + KCN \rightarrow CH_3CH_2CN + KBr$

$CH_3CH_2Br + AgCN \rightarrow CH_3CH_2NC + KBr$

Like KCN, KNO_2 form R-ONO while $AgNO_2$ produces $R\text{-}NO_2$ as product.

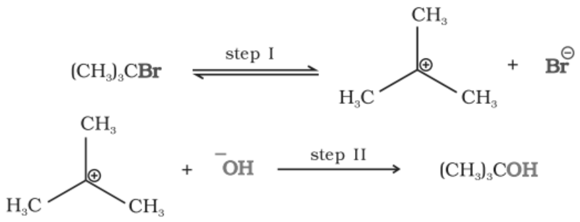
Nucleophilic substitution reactions: These are of two types:

(1) S_N1 (Substitution, Nucleophilic, Unimolecular): In such type of reactions, rate = k [RX] i.e., rate is independent of concentration of nucleophile and occurs in two steps. Such reactions are favoured by polar solvents.

(2) S_N2 (Substitution, Nucleophilic, bimolecular): (i) In such type of reactions, rate = k [RX] $[Nu]^-$, i.e., rate of reaction depends on concentration of nucleophile and take place in one step.

(ii) A S_N2 reaction proceeds with complete Stereochemical inversion while a S_N1 reaction proceeds with racemisation.

(a) S_N1 type (Unimolecular Nucleophilic reactions proceed in two steps: ref. ncert

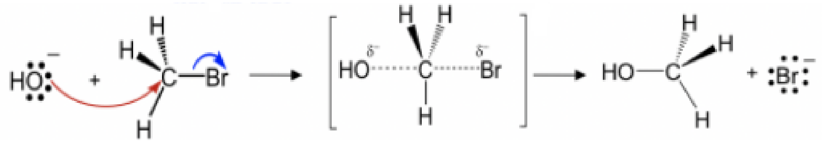


Rate, r = k [RX]. It is a first order reaction.

Reactivity order of alkyl halide towards S_N1 mechanism 3° > 2° > 1° Polar solvents, low concentration of nucleophiles and weak nucleophiles favour S_N1 mechanism.

In S_N1 reactions, partial racemisation occurs due to the possibility of frontal as well as backside attack on planar carbocation.

(b) S_N2 type (Bimolecular Nucleophilic substitution): These reactions proceed in one step.



It is a second order reaction with r = k[RX] [Nu].

During S_N2 reaction, inversion of configuration occurs (Walden inversion) i.e., starting with dextrorotatory halide a laevo product is obtained and vice-versa, e.g.,

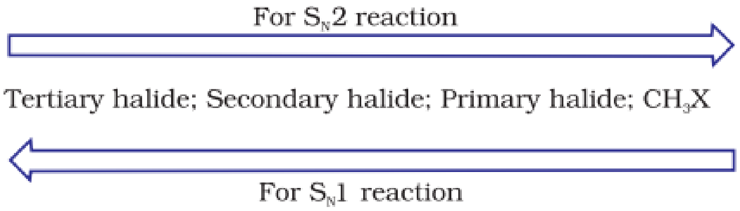
Reactivity of halides towards S_N2 mechanism is 1° > 2° > 3°

Rate of reaction in S_N2 mechanism depends on the strength of the attacking nucleophile. Strength of some common nucleophiles is

$: CN^- >: I^- >: OR^- >: OH^- > CH_3COO: > H_2O > F^-$

Non-polar solvents, strong nucleophiles and high concentration of nucleophiles favour S_N2 mechanism.

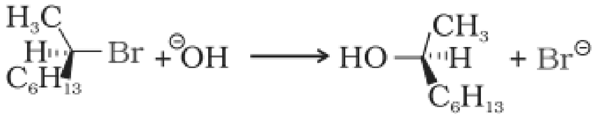
Order of reactivity of alkyl halides towards SN1 and SN2 as follows: ref. ncert



Stereochemical Aspects of Nucleophilic Substitution Reactions

(a) Stereochemical Aspects of SN2 reaction:

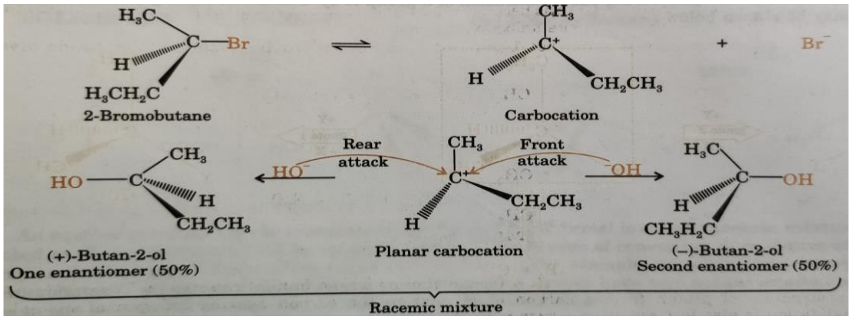
In case of optically active alkyl halides, the product formed as a result of SN2 mechanism has the inverted configuration as compared to the reactant. This is because the nucleophile attaches itself on the side opposite to the one where the halogen atom is present. When (–)-2-bromooctane is allowed to react with sodium hydroxide, (+)-octan-2-ol is formed with the –OH group occupying the position opposite to what bromide had occupied. (Ref. ncert)



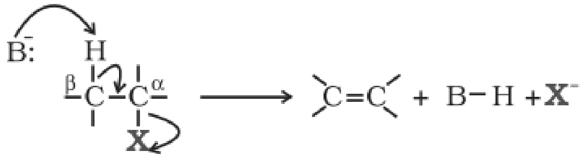
Thus, SN 2 reactions of optically active halides are accompanied by inversion of configuration.

(b) Stereochemical Aspects of SN1 reaction:

In case of optically active alkyl halides, SN1 reactions are accompanied by racemization. Actually, the carbocation formed in the slow step being sp^2 hybridized is planar (achiral). The attack of the nucleophile may be accomplished from either side of the plane of carbocation 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. (Ref. ncert)



(b) Elimination reaction: When a haloalkanes with β-halogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from α-carbon and a halogen atom from the a-carbon atom.



B=Base ; **X**=Leaving group

Ease of dehydrohalogenation among halides 3° > 2° > 1°

Reaction with metals:

$$CH_3CH_2Br + \xrightarrow{\text{Mg dry ether}} CH_3CH_2MgBr \text{ (Grignard reagent)}$$

$$CH_3CH_2MgBr + H_2O \rightarrow CH_3CH_3 + Mg\,(OH)Br$$

Wurtz reaction: $2RX + 2Na \rightarrow RR + 2NaX$

Isomerisation: $CH_3CH_2CH_2 – Cl \xrightarrow{573\ K} CH_3 – CH(Cl) – CH_3$

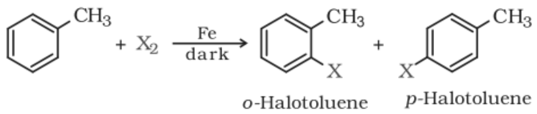
Relative reactivity of alkyl halides for same alkyl group is: RI > RBr > RCI > RF

Methods of preparation of Haloarenes. Haloarenes can be prepared by side chain halogenation or nuclear halogenation of aromatic hydrocarbons.

1. By Halogenation of Aromatic Hydrocarbons:

$$C_6H_6 + Cl_2 \xrightarrow{\text{FeCl3, dark}} C_6H_5Cl + HCl$$

It is an electrophilic substitution reaction.



2. By Side Chain Halogenation:

$$C_6H_5CH_3 + Cl_2 \xrightarrow{\text{sunlight}} C_6H_5CH_2Cl + Cl_2 \xrightarrow{\text{sunlight}} C_6H_5CHCl_2 + Cl_2 \xrightarrow{\text{sunlight}} C_6H_5CCl_3$$

(It involves free radical mechanism.)

3. From diazonium salts:

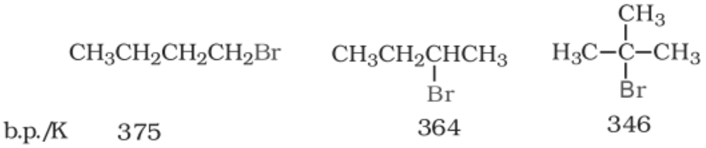
(i) By Sandmeyer reaction: $C_6H_5\ N_2^+Cl^- \xrightarrow{\text{CuCl/HCl}} C_6H_5\ Cl + N_2$

(ii) By Gattermann reaction: $C_6H_5\ N_2^+Cl^- \xrightarrow{\text{Cu/HCl}} C_6H_5\ Cl + N_2$

4. From Phenol: $C_6H_5OH + PCl_5 \xrightarrow{\quad\quad} C_6H_5Cl + HCl + POCl_3$

Physical Properties of Aryl Halides:

1. Aryl halides are colourless liquids or crystalline solids..
2. Boiling point generally increases with increase in the size of aryl group or halogen atom. Boiling point order Ar – I > Ar – Br > Ar – Cl > Ar – F, the boiling points of isomeric haloalkanes decrease with increase in branching (ncert)



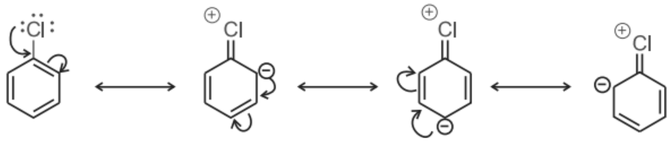
3. The melting point of p -isomer is more than o- and m-isomer. This is because of more symmetrical nature of p-isomer.
4. Due to resonance in Chlorobenzene, C-CI bond is shorter and hence, its dipole moment is less than that of cyclohexyl chloride.

Chemical Properties of Aryl Halides:

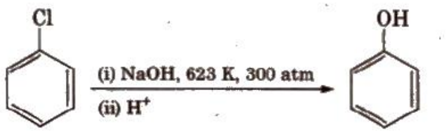
1. Nucleophilic Substitution Reaction

Aryl halides are less reactive towards Nucleophilic substitution reaction. Their low reactivity is attributed due to the following reasons:

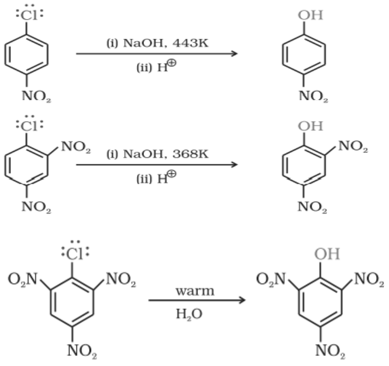
1. Due to resonance, C-X bond has partial double bond character.
2. Stabilisation of the molecule by delocalisation of electrons.
3. Instability of phenyl carbocation.



However, aryl halides having electron withdrawing groups (like – NO_2, -SO_3H, etc.) at ortho and para positions undergo Nucleophilic substitution reaction easily.



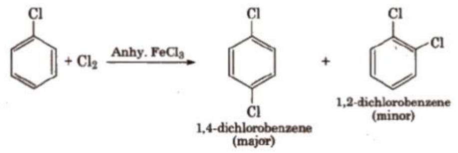
Presence of electron withdrawing group (-NO_2) increases the reactivity. (ref. ncert)



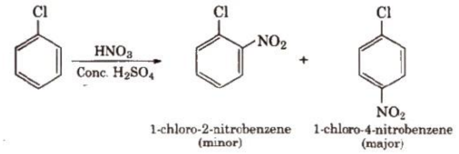
2. Electrophilic Substitution Reactions

Halogens are deactivating but o, p-directing. Thus, chlorination, nitration, Sulphonation and Friedel Craft's reaction give a mixture of o- and p- Chloro substituted derivatives.

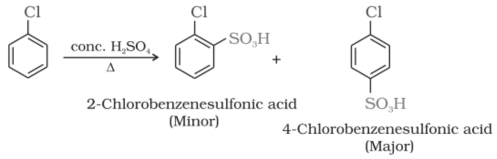
(i) Halogenation:



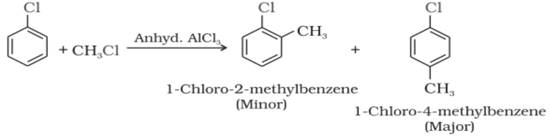
(ii) Nitration:

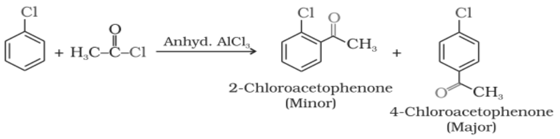


(iii) Sulphonation:



(iv) Friedel-Crafts reaction: Alkylation and Acylation:

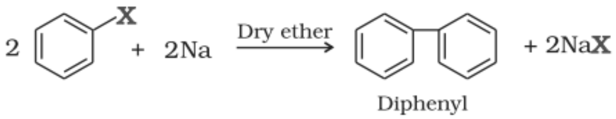




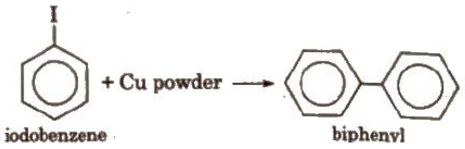
3. Reaction with Metals:

(i) Wurtz Fittig reaction:

(ii) Fitting reaction:

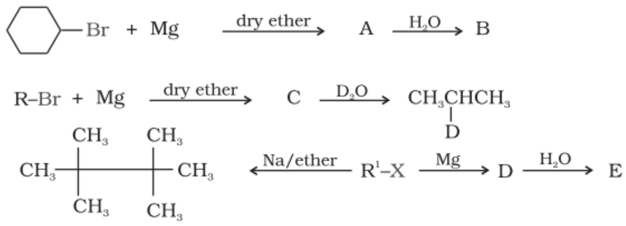


(iii) Ullmann reaction: Iodobenzene reacts with copper powder to form biphenyl



Example:

10.9 Identify A, B, C, D, E, R and R^1 in the following:



A = Cyclohexyl magnesium bromide, B = Cyclohexane, C = RMgBr
D = $(CH_3)_3$MgBr, E = 2-Methyl propane, R' = $(CH_3)_3C$ -

Polyhalogen Compounds:

Dichloromethane (Methylene chloride), CH_2Cl_2: It is a colourless, sweet smelling liquid.
It 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) $CHCl_3$: It is a colourless oily liquid with a peculiar sickly smell and a burning taste. It is heavier than water. It is sparingly soluble in water but readily soluble in organic solvent such as ethanol and ether. It is poisonous compound. The vapour when inhaled cause consciousness. Due to this reason, chloroform is used as anaesthetic. It is used in medicine and used in the production of Freon refrigerant. It is used as a laboratory reagent.
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.

$$2CHCl_3 + O_2 \longrightarrow 2COCl_2 + 2HCl$$

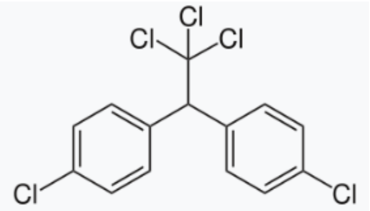
Carbonyl chloride (phosgene)

Tetrachloromethane (Carbon tetrachloride) CCl_4: It is a colourless oily liquid with sickly smell.
It is insoluble in water but soluble in organic solvent such as ethanol and ether. It is inflammable.
It is used in the manufacture of refrigerants and propellants for aerosol cans.
It is also used as feedstock in the synthesis of chlorofluorocarbons (Freons) and other chemicals.
It is also used as a solvent in manufacturing of pharmaceuticals.
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.
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.

Triiodomethane (Iodoform) CHI_3: It is a yellow coloured crystalline solid. It is insoluble in water but soluble in organic solvent such as ethanol and ether.
It is used as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to Iodoform itself.
It is used in the manufacturing of pharmaceuticals.

Freons: The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. They are extremely stable, unreactive, non-toxic, noncorrosive and easily liquefiable gases.
Freon 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.

p, p'-Dichlorodiphenyltrichloroethane (DDT): DDT, the first chlorinated organic insecticides, was originally prepared in 1873.Paul Muller was awarded the Nobel Prize in Medicine and Physiology in 1948 for this discovery.
It is synthesized by heating a mixture of chloral (1 mol) with Chlorobenzene (2 mol) in the presence of conc. H_2SO_4.
$Cl_3C\text{-}CHO + C_6H_5\,Cl \xrightarrow{\text{conc. H2SO4}} \text{DDT}$

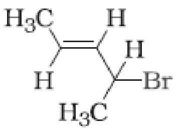


DDT is a powerful insecticide. It is widely used as an insecticide for killing mosquitoes and other insects.

ASSIGNMENTS:

Q1. 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.
Ans. $CH_3CH_2CH_2CH_2CH_2Br$ 1-Bromopentane (primary)
$CH_3CH_2CH_2CH\ (Br)\ CH_3$ 2-Bromopentane (secondary)
$CH_3CH_2CH\ (Br)\ CH_2\ CH_3$ 3-Bromopentane (secondary)
$(CH_3)_2CHCH_2CH_2Br$ 1-Bromo-3-methylbutane (primary)
$(CH_3)_2CHCHBrCH_3$ 2-Bromo-3-methylbutane (secondary)
$(CH_3)_2CBrCH_2CH_3$ 2-Bromo-2-methylbutane (tertiary)
$CH_3CH_2CH\ (CH_3)\ CH_2Br$ 1-Bromo-2-methylbutane (primary)
$(CH_3)_3CCH_2Br$ 1-Bromo-2, 2-dimethylpropane (primary)

Q2. Write IUPAC names of the following:

(i)


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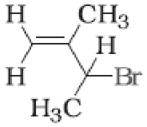
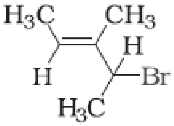
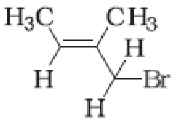
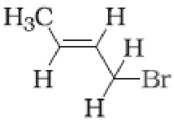
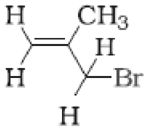


(iii)


(iv)


(v)


(vi)


Ans.

(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

Q3. Why is Sulphuric acid not used during the reaction of alcohols with KI?
Ans. Sulphuric acid is an oxidising agent. It will oxidise HI produced during the reaction to I_2 and therefore, will prevent reaction between an alcohol and HI to form alkyl halide.

Q4. Write structures of different dihalogen derivatives of propane.
Ans. 1,1-dibromopropane, 1,2-dibromopropane, 1,3-dibromopropane, 2,2-dibromopropane

Q5. Arrange each set of compounds in order of increasing boiling points.
(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.
(ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.
Ans. (i) Chloromethane < Bromomethane < Dibromomethane < Bromoform
(ii) Isopropyl chloride < 1-Chloropropane < 1-Chlorobutane

Q6. Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain.
Ans. KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C—C bond is more stable than C—N bond. However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.

Q7. In the following pairs of halogen compounds, which would undergo SN^2 reaction faster?
(i) C_6H_{11}-CH_2Cl and C_6H_{11}-Cl
(ii) $CH_3CH_2CH_2CH_2I$ and $CH_3CH_2CH_2CH_2Cl$
Ans. (i) C_6H_{11}-CH_2Cl is primary halide and therefore undergoes SN^2 reaction faster.
(ii) $CH_3CH_2CH_2CH_2I$ will undergoes SN^2 reaction faster because iodide ion is a better leaving group because of its large size, it will be released at a faster rate in the presence of incoming nucleophile.

Q8. Predict the order of reactivity of the following compounds in SN^1 and SN^2 reactions:
(i) The four isomeric bromobutanes
(ii) $C_6H_5CH_2Br$, $C_6H_5CH\ (C_6H_5)\ Br$, $C_6H_5\ CH\ (CH_3)\ Br$, $C_6H_5\ C\ (CH_3)\ (C_6H_5)\ Br$

Ans. In SN^1 reaction, stability of carbocation decreases, tertiary > secondary > primary
(i) $CH_3CH_2CH_2CH_2Br < (CH_3)_2CHCH_2Br < CH_3CH_2CH\ (Br)\ CH_3 < (CH_3)_3CBr$ (SN^1)
$CH_3CH_2CH_2CH_2Br > (CH_3)_2CHCH_2Br > CH_3\ CH_2\ CH\ (Br)\ CH_3 > (CH_3)_3CBr$ (SN^2)
(ii) $C_6H_5\ C\ (CH_3)\ (C_6H_5)\ Br > C_6H_5\ CH\ (C_6H_5)\ Br > C_6H_5\ CH\ (CH_3)\ Br > C_6H_5CH_2Br$ (SN^1)
$C_6H_5\ C\ (CH_3)\ (C_6H_5)\ Br < C_6H_5\ CH\ (C_6H_5)\ Br < C_6H_5\ CH\ (CH_3)\ Br < C_6H_5CH_2Br$ (SN^2)

Q9. 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?

Ans. (i) Due to magnitude of negative charge (δ-) is less on Cl atom of Chlorobenzene than in cyclohexyl chloride.

(ii) Alkyl halides, though polar, are immiscible with water because the molecules of water are held together by hydrogen bonds.

(iii) Grignard reagents are very reactive.

Q10. Primary alkyl halide C_4H_9Br (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.

Ans. (a) isobutyl bromide
(b) 2-methyl prop-1-ene
(c) t-butyl bromide
(d) 2, 5-dimethyl hexane.