

HALOALKANES

Compounds having one or more halogen atoms bonded to sp^3 hybridised carbon of alkane.



(X = F, Cl, Br, I)

CLASS XII CHEMISTRY**HALOALKANES AND HALOARENES**

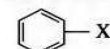
Organic compounds containing halogen (F, Cl, Br, I) as the functional group.

GENERAL POINTS

- Haloalkanes are more reactive than haloarenes.
- Reactivity order (R-X) in nucleophilic substitution: $RI > RBr > RCl > RF$
- Bond strength (C-X) order: $R-F > R-Cl > R-Br > R-I$

HALOARENES

Compounds having one or more halogen atoms bonded to sp^2 hybridised carbon of aromatic ring.



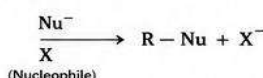
(X = F, Cl, Br, I)

A. HALOALKANES (R-X)**1. PHYSICAL PROPERTIES**

- Colourless compounds.
- Lower members (C_1-C_4) are gases, C_5-C_{17} are liquids and higher members are solids.
- Boiling points are higher than corresponding alkanes but lower than corresponding alcohols.
- Insoluble in water but soluble in organic solvents.
- Density greater than water.

2. CHEMICAL PROPERTIES

Undergo mainly nucleophilic substitution reactions.

**3. IMPORTANT REACTIONS****(i) Nucleophilic Substitution Reactions**

- With aqueous KOH (hydrolysis)

$$R-X + KOH(aq) \longrightarrow R-OH + KX$$

(Alcohol)
- With alcoholic KOH (dehydrohalogenation)

$$R-CH_2-CH_2-X + alc. KOH \longrightarrow R-CH=CH_2 + KX + H_2O$$

(Alkene)
- With sodium ethoxide (Williamson synthesis)

$$R-X + C_2H_5ONa \longrightarrow R-OC_2H_5 + NaX$$

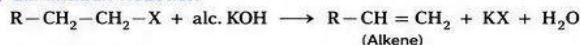
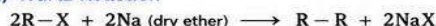
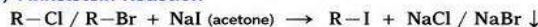
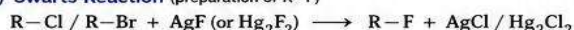
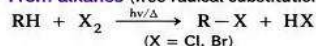
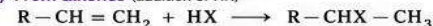
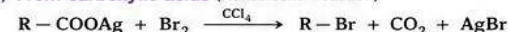
(Ether)
- With KCN (nitrile)

$$R-X + KCN \longrightarrow R-CN + KX$$

(Nitrile)
- With $AgNO_3$ (precipitation)

$$R-X + AgNO_3(alc.) \longrightarrow R-ONO_2 + AgX \downarrow$$

(White ppt.)

(ii) Elimination Reaction**(iii) Wurtz Reaction****(iv) Finkelstein Reaction****(v) Swarts Reaction (preparation of R-F)****4. PREPARATION OF HALOALKANES****(i) From alkanes (free radical substitution)****(ii) From alcohols****(iii) From alkenes (addition of HX)****(iv) From carboxylic acids (Hunsdiecker reaction)****USES OF HALOALKANES**

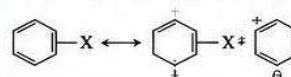
- As solvents ($CHCl_3, CCl_4$).
- As refrigerants (Freons).
- As anaesthetics ($CHCl_3$).
- In fire extinguishers (CF_2Cl_2).
- As intermediates in organic synthesis.

**B. HALOARENES (Ar-X)****1. PHYSICAL PROPERTIES**

- Generally colourless solids or liquids with characteristic odour.
- Boiling points are higher than corresponding arenes.
- Insoluble in water but soluble in organic solvents.
- Denser than water.

2. CHEMICAL PROPERTIES

Undergo mainly electrophilic aromatic substitution reactions. The C-X bond is stronger and has partial double bond character due to resonance, hence less reactive towards nucleophilic substitution.

**3. IMPORTANT REACTIONS****(i) Electrophilic Substitution Reactions**

- Nitration

$$Ar-X + HNO_3 \xrightarrow{conc. H_2SO_4} o-, p-NO_2-Ar-X + H_2O$$
- Sulphonation

$$Ar-X + SO_3 / fuming H_2SO_4 \longrightarrow o-, p-SO_3H-Ar-X + H_2O$$
- Halogenation

$$Ar-X + X_2 \xrightarrow{FeX_3 (cat.)} o-, p-X-Ar-X + HX$$
- Friedel-Crafts Alkylation

$$Ar-X + RCl \xrightarrow{anhyd. AlCl_3} o-, p-R-Ar-X + HCl$$
- Friedel-Crafts Acylation

$$Ar-X + RCOCl \xrightarrow{anhyd. AlCl_3} o-, p-RCO-Ar-X + HCl$$

(ii) Nucleophilic Substitution Reactions (Under drastic conditions)

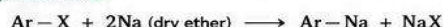
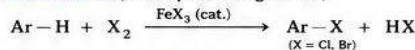
- Hydrolysis (Dow process)

$$Ar-Cl + NaOH(aq) \xrightarrow{623 K, 300 atm} Ar-OH + NaCl$$

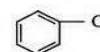
(Phenol)
- With $NaNH_2$ (high temperature)

$$Ar-Cl + 2NaNH_2 \xrightarrow{623 K} Ar-NH_2 + NaCl + NH_3$$

(Aniline)

(iii) Metalation**4. PREPARATION OF HALOARENES****(i) From arenes (electrophilic halogenation)****(ii) From diazonium salts (Sandmeyer reaction)****(iii) From phenols****USES OF HALOARENES**

- As intermediates in dyes, drugs and pesticides.
- In manufacturing of polymers, plastics and pharmaceuticals.
- Chlorobenzene is used as solvent and in production of DDT.

**KEY POINTS**

- Haloalkanes: More reactive, undergo nucleophilic substitution easily.
- Haloarenes: Less reactive, undergo electrophilic substitution; C-X bond has partial double bond character.

QUESTION BANK

SECTION – A (1 MARK)

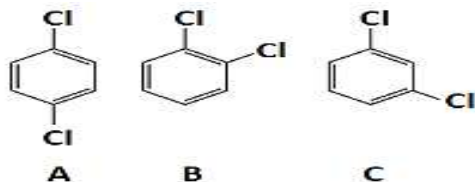
1. Oxidation of chloroform by air in the presence of sunlight produces a poisonous gas known as :
(ALL INDIA 2026)
(a) Mustard gas (b) Tear gas (c) Chlorine gas (d) Phosgene gas
2. Which of the following haloalkanes react with aqueous KOH most rapidly by S_N1 reaction?
(ALL INDIA 2025)
(A) 2-Chlorobutane (B) 1-Bromobutane
(C) 2-Bromo-2-Methylpropane (D) 2,2-Dimethyl-1-Chloropropane
3. 2-Bromo-2-methylpropane is allowed to react with alcoholic KOH solution. The major product formed is –
(ALL INDIA 2022)
(a) $(CH_3)_2C=CH_2$ (b) $CH_3-CH=CH-CH_3$ (c) $(CH_3)_2CH-CH_3$ (d) $CH_3-CH_2-CH_2-CH_3$

4. Given below are two statements:

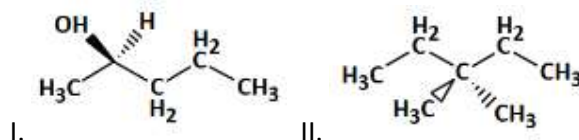
Statement 1: The process of conversion of enantiomer into a racemic mixture is known as racemization.

Statement 2: 1-chlorobutane has a higher boiling point than 2-chlorobutane.

- (a) Statement 1 is **true** and statement 2 is **false**
(b) Statement 1 is **false** and statement 2 is **true**.
(c) Both statement 1 and statement 2 are **false**.
(d) Both statement 1 and statement 2 are **true**.
5. Match Column I (Compounds) with Column II (Uses), and mark the appropriate option:
- | Column I (Compounds) | Column II (Uses) |
|--------------------------|---|
| (A) Carbon tetrachloride | (i) Paint remover |
| (B) Methylene chloride | (ii) Refrigerators and air conditioners |
| (C) DDT | (iii) Fire extinguisher |
| (D) Freons | (iv) Non-biodegradable insecticide |
- (a) (A)=(ii), (B)=(iii), (C)=(i), (D)=(iv) (b) (A)=(iv), (B)=(iii), (C)=(ii), (D)=(i)
(c) (A)=(i), (B)=(ii), (C)=(iii), (D)=(iv) (d) (A)=(iii), (B)=(i), (C)=(iv), (D)=(ii)
6. What is the correct order of dipole moments from highest to lowest among the following?
(a) $CH_3Cl > CH_3Br > CH_3F$ (b) $CH_3Cl > CH_3F > CH_3Br$
(c) $CH_3Br > CH_3Cl > CH_3F$ (d) $CH_3Br > CH_3F > CH_3Cl$
7. The correct order of melting point for the given compounds is:



- (a) $A > B > C$ (b) $A > C > B$ (c) $B > A > C$ (d) $C > A > B$
8. Consider the following compounds:



Identify the correct statement related to these compounds.

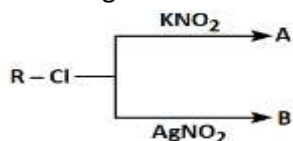
(a) I and II are chiral.

(b) I and II are achiral.

(c) I is chiral and II is achiral.

(d) I is achiral and II is chiral.

9. Consider the following reactions:



The relation between A and B are:

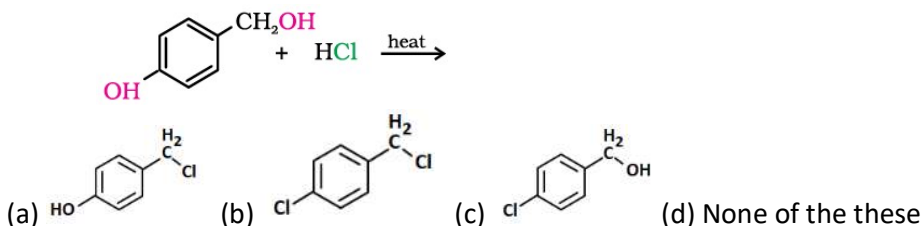
(a) Enantiomers

(b) Functional group isomers

(c) Position isomers

(d) Identical compounds

10. Examine the given reaction and predict the structure of the major monohalo product.



ASSERTION REASON TYPE QUESTIONS (1 MARKS)

These questions are based on Assertion-Reason and write the correct option from the following four options given:

(a) Both A and R are correct and R is the correct explanation of A.

(b) Both A and R are correct but R is not the correct explanation of A.

(c) A is correct and R is not correct.

(d) A is not correct but R is correct

11. **Assertion (A):** undergoes S_N2 reaction faster than .

Reason(R): Iodine is a better leaving group because of its larger size.

12. **Assertion (A):** Aryl halides and vinyl halides are less reactive than alkyl halides and are not easily hydrolyzed.

Reason (R): The cleavage bond in aryl halides acquires a double bond character due to resonance, which makes its cleavage difficult.

13. **Assertion (A):** Grignard's reagent reaction occurs in aqueous medium.

Reason (R): In the presence of water, Grignard's reagent gets destroyed.

14. **Assertion (A):** AgCN gives alkyl isocyanides (R-NC) as the major product in nucleophilic substitution reactions with alkyl chloride.

Reason (R): AgCN is predominantly covalent, allowing the nitrogen atom to act as the nucleophile.

15. **Assertion (A):** The S_N2 reaction of (-)-2-bromooctane with sodium hydroxide gives (+)-octan-2-ol with inversion of configuration.

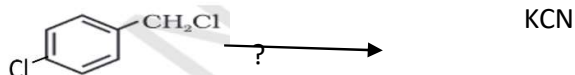
Reason(R): S_N2 reactions proceed through a carbocation intermediate which allows for the inversion of configuration.

Answer Key

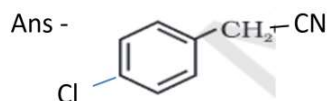
1	2	3	4	5	6	7	8	9	10
(d)	(c)	(a)	(d)	(d)	(b)	(a)	(c)	(b)	(a)
11	12	13	14	15					
(a)	(a)	(d)	(a)	(c)					

SECTION - B (2MARKS)

1. Consider the following reaction: (ALL INDIA 2024)



The major product to the reaction is



2. An alkyl halide (A) of molecular formula $\text{C}_6\text{H}_{13}\text{Cl}$ on treatment with alcoholic KOH gives two isomeric alkenes (B) and (C) of molecular formula C_6H_{12} . Both alkenes on hydrogenation gives 2,3-dimethylbutane. Write the structures of (A), (B) and (C) (ALL INDIA 2023)

(HINT: A. **2-chloro-2,3-dimethylbutane**, B **2,3-dimethylbut-1-ene**, C, **2,3-dimethylbut-2-ene**.)

3. Chlorobenzene and benzyl chloride are both aromatic halo compounds, but they react differently with alcoholic silver nitrate solution. Explain how you can distinguish between the two using this reagent.

(Hint: Due to resonance aryl halide is less reactive towards nucleophilic substitution reaction.)

4. Draw the structures of major product(s) in each of the following reactions : $2 \times 1 = 2$

(a) $\text{C}_6\text{H}_5\text{-Br} + \text{Mg}$ (Ether)----- ?

(b) $\text{CH}_3\text{-CH}_2\text{-Br} + \text{AgCN}$ -----?

(HINT (a) $\text{C}_6\text{H}_5\text{-Mg-Br}$

(c) $\text{CH}_3\text{-CH}_2\text{-NC} + \text{AgBr}$

5. Apply your understanding of solubility and intermolecular forces to explain why alkyl halides are insoluble in water despite having polar bonds.

(Hint: Unable to form hydrogen bonds with water molecules)

SECTION – C (3 MARKS)

1. Answer the following : $3 \times 1 = 3$ (ALL INDIA 2026)

(a) Which isomer of $\text{C}_4\text{H}_9\text{Br}$ is most reactive towards $\text{S}_{\text{N}}1$ reaction ?

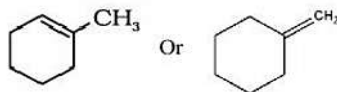
(b) Predict the alkene that would be formed by dehydrohalogenation of 1-Bromo-1-methylcyclohexane.

Although chlorine shows strong – I effect, yet it is ortho- and para-directing in electrophilic aromatic substitution reactions. Why ?

(Hint-

(a) Tert-butyl bromide / $(\text{CH}_3)_3\text{CBr}$ / 2-Bromo-2-methylpropane

(b)



(c) Because +R effect stabilises the intermediate carbocation.

2. A compound (A) with molecular formula $\text{C}_4\text{H}_9\text{I}$ which is a primary alkyl halide, reacts with alcoholic KOH to give compound (B). Compound (B) reacts with HI to give (C) which is an isomer of (A). When (A) reacts with Na metal in the presence of dry ether, it gives a compound (D), C_8H_{18} which is different from the compound formed when n-butyl iodide reacts with sodium. Write the structures of (A), (B), (C) and (D). Write the chemical equation when compound (A) is reacted with alcoholic KOH. (ALL INDIA 2025)

(HINT, (A,) **Isobutyl iodide** (1-Iodo-2-methylpropane), (B); **2-methylpropene** (Isobutylene)

(C): 2-iodo-2-methylpropane (tert-butyl iodide) , (D): 2,5-dimethylhexane,

3. Explain why resonance and electron-withdrawing groups to explain why p-nitrochlorobenzene undergoes nucleophilic substitution faster than chlorobenzene. Support your answer with appropriate resonating structures.

(Hint: In this reaction a carbanion intermediate is formed which is stabilized by –R effect (resonance) as well as –I effect of NO₂ group.)

4. Prop-1-ene undergoes electrophilic addition reaction in the presence of HBr.

(i) Write the **names of all products** formed in the reaction.

(ii) Identify the **major product** and explain **why it is formed in greater amount**.

5. (a) Study the reaction below and answer the questions that follow:



(i) Suggest a way to increase the rate of the forward reaction in the given process.

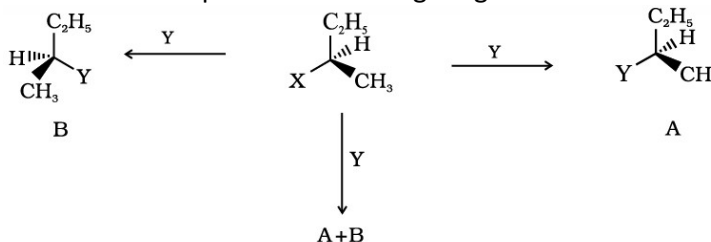
(ii) If ethyl fluoride is to be prepared, which reaction should be used?

(b) Out of  and , which is an example of benzyl halide.

SECTION – D CASE BASED QUESTIONS (4 MARKS)

1. Read the passage given below and answer the following questions:

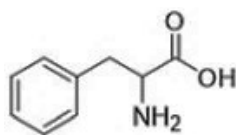
When a chemical reaction occurs at an **asymmetric carbon atom**, the spatial configuration around that carbon may change depending on the mechanism of the reaction. In the replacement of a group **X** by another group **Y**, three outcomes are possible. The image is given below:



(i) In the given reaction, if compound B is the only product formed, what type of configuration change has occurred?

- (a) Retention of configuration (b) Inversion of configuration
(c) Racemisation (d) No change in configuration

(ii) Observe the compound shown in the image given below and determine how many **chiral centers** are present in the molecule



(iii) If compounds A and B are present in equal proportions, will the resulting mixture be optically active or optically inactive? **Explain your answer.**

2. Read the passage given below and answer the following questions:

When a **haloalkane** containing a **β-hydrogen atom** is heated with alcoholic potassium hydroxide (KOH), it undergoes **β-elimination**, where a hydrogen atom is removed from the β-carbon and a halogen atom is removed from the α-carbon. This results in the formation of an **alkene**. Elimination reactions follow the order of reactivity:

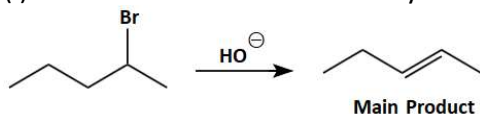
Tertiary (3°) > Secondary (2°) > Primary (1°).

If more than one β-hydrogen is available, multiple alkenes may be formed. In such cases, the **major product** follows **Zaitsev's (Saytzeff) Rule**, which states that:

"In dehydrohalogenation reactions, the preferred product is the alkene with the greater number of alkyl groups attached to the doubly bonded carbon atoms."

For example, in the elimination of 2-bromopentane, the major product is **pent-2-ene**, which is more substituted and thus more stable.

(i) Select the correct statement by considering the following reaction:



- (a). Hydroxide ion is a base. (b). Hydroxide ion is a nucleophile.
(c). It is a nucleophilic addition reaction. (d). It is a nucleophilic substitution reaction.

(Hint: hydrogen atom is removed from the β -carbon by base)

(ii) Predict the major product formed when 2-chloro-2-methylpropane is heated with alcoholic potassium hydroxide.

(Hint: Follow the mechanism of elimination reaction given in summary)

(iii) Out of 2-bromopentane, 2-bromo-2-methylbutane and 1-bromopentane, which compound is most reactive towards elimination reaction and why ?

(Hint: Elimination reaction order $3^\circ > 2^\circ > 1^\circ$)

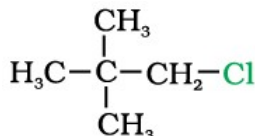
SECTION –E (5 MARKS)

1. (a) Starting with ethane, how could the following compounds be prepared?

- (i). Propanenitrile; (ii). Ethyl benzene

(Hint: Halogenation, followed by nucleophilic substitution; Halogenation, followed by Friedel-Craft alkylation)

(b) Provide the IUPAC name of the given compound



2. (a) A common lab solvent can cause liver and kidney damage with prolonged exposure. When exposed to air and light, it slowly forms a highly toxic gas. To prevent this, it is stored in sealed, dark-coloured bottles.

(i) Name the poisonous gas formed.

(ii) Write the chemical reaction involved in its formation.

(Hint: Gas is phosgene; formula is COCl_2)

(b) A student is asked to prepare an aromatic-alkyl hydrocarbon in the lab. They use a mixture of an aryl halide and an alkyl halide, along with metallic sodium in dry ether. The reaction produces a compound used in fuels and perfumes.

(i) Name the reaction taking place in this case.

(ii) Write the balanced chemical equation for the reaction between bromobenzene and methyl bromide.

Hint: (Wurtz-Fittig reaction)

3. How the following conversions can be carried out?

- (a) Propene to propan-1-ol
(b) Ethanol to propanenitrile
(c) Ethyl chloride to propanoic acid
(d) Aniline to chlorobenzene