

HALOALKANES AND HALOARENES-II PUC

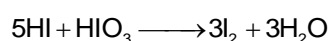
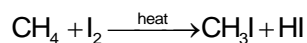
- ⊙ Organic halogen compounds are compounds which contain one or more halogen atoms directly attached to the carbon atoms. They may be attached to the same carbon or different carbon atoms.
- ⊙ Alkyl halides (Haloalkanes) are the mono halogen derivatives of alkanes. They have the general formula $C_nH_{2n+1}X$ where X is the halogen atom.
- ⊙ Based on the type of carbon atom to which the halogen atom is attached haloalkanes are classified into 3 types.
The different types of haloalkanes are primary, secondary and tertiary haloalkanes.
- ⊙ In haloalkanes, the carbon atom to which the halogen is attached is sp^3 hybridised.
- ⊙ Haloalkane is the name of mono halogen derivatives of alkanes in the IUPAC system of naming.

1. By Direct Halogenation of Alkanes:

When alkanes are treated with halogen, chlorine or bromine, in the presence of light or heat, a mixture of mono and poly substituted products is obtained.

In general, the ease of substitution of different types of hydrogen atoms follows the order—benzylic > allylic > tertiary > secondary > primary > vinylic, aryl.

The iodination of alkanes is reversible and is done by heating the alkane with iodine in the presence of oxidizing agents like conc. HNO_3 , HIO_4 or HIO_3 . The function of using such agents is to oxidize HI, formed during the reaction, to iodine, and hence shift the equilibrium in the forward direction.



2. By Addition of HX on Alkenes (HX = HCl, HBr, HI):

In unsymmetrical alkenes the addition of halogen acids takes place according to the Markonikov's rule. Anti-Markonikov's addition is observed during addition of HBr in presence of peroxide (H_2O_2), known as peroxide effect or Kharasch effect.

3. From Alcohols:

a) Action of halogen acids: Primary alcohols need $ZnCl_2$ (anhydrous) for preparation of alkyl halides. The mixture of HCl and anhydrous $ZnCl_2$ is known as Lucas reagent.

This reaction is also known as Groves process.

Bromoalkanes can be obtained by heating alcohols with KBr or NaBr and conc. H_2SO_4 . HBr is generated in situ.

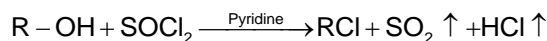
Iodoalkanes are obtained by heating alcohols with KI and 95% H_3PO_4 .

The reactivity order of alcohols is tertiary > secondary > primary and the reactivity order of halogen is $HI > HBr > HCl$.

b) By reaction with phosphorus halides:

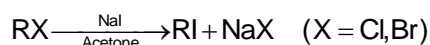
Chloroalkanes are obtained by reaction of alcohols with PCl_3 or PCl_5 .

c) Action of Thionyl Chloride or Darzen's Method:



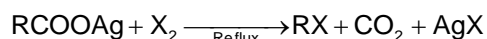
4) By Halide Exchange:

(Finkelstein reaction) Iodides are usually prepared by this method.

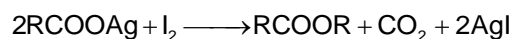


5) From Silver Salts of Fatty Acids (Borodin–Hunsdiecker reaction):

Alkyl chlorides and alkyl bromides are obtained by the action of Cl_2 or Br_2 in CCl_4 on silver salt of fatty acids. The reaction proceeds through free radical mechanism.



Iodoalkanes, cannot be obtained by this method because I_2 reacts with silver salts of fatty acids to form ester.



Physical properties of alkylhalides (haloalkanes):

- Physical state:** CH_3Cl , C_2H_5Cl , CH_3Br are gases at room temperature. The alkyl halide upto C_{18} are liquids, while higher are colourless solids.
- Boiling point:** The boiling point of haloalkanes are in the order $RCl < RBr < RI$. It is because with the increase in size and mass of the halogen atom, the magnitude of van der Waals forces of attraction increases. Among isomeric alkyl halides, the boiling point decreases with increase in branching in the alkyl group. This is due to the reason that with increase in branching the molecule acquire less surface area due to attainment of spherical shape. As a result, interparticle forces become weaker, resulting in lower boiling point.

The boiling point of various halogen compounds increases with the increase in number of halogen atoms.

The boiling point of alkyl halides shows following order,

Alkyl iodide > Alkyl bromide > Alkyl chloride (for a given alkyl group)

Methyl halide < Ethyl halide < Propyl halide (for a given halide)

1° halide > 2° halide > 3° halide (for a given halide and alkyl group).

- Solubility:** The alkyl halides are polar in nature but still they are insoluble in water as they do not form H-bonds with water molecules.
- Density:** Alkyl fluorides and alkyl chlorides are lighter than water. Alkyl bromides and alkyl iodides are heavier than water. The density of halides thus follow the order, iodide > bromide > chloride > fluoride.

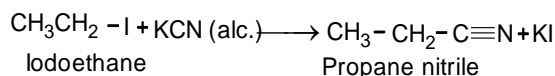
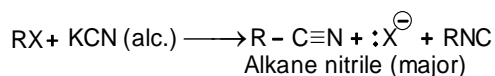
I. Nucleophilic Substitution of alkyl halides:

The halogen atom of alkyl halide is easily replaced by a nucleophile to give a large variety of nucleophilic substitution reactions.

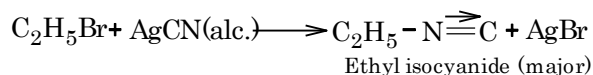
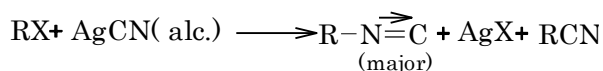
1) **Replacement by hydroxyl group** (formation of alcohols):

2) **Replacement by alkoxy group:** (formation of ethers). In this reaction, alkyl halide is treated with alcoholic sodium or potassium alkoxide to form ether. This reaction is known as Williamson's synthesis.

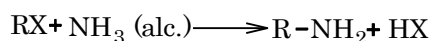
3) **Replacement by cyano group** (formation of cyanides or nitriles):



4) **Replacement with Isocyanide** (formation of isocyanide):



5) **Replacement by amino group** (formation of amines). This reaction is known as Hofmann's ammonolysis.



6) **Replacement by nitro group.** Treatment of alkyl halide with AgNO_2 gives nitro alkane as a major product.

7) **Replacement with nitrite group.** Treatment of alkyl halide with potassium nitrite gives alkyl nitrite as a major product.

8) **Replacement with -SH (hydrosulphide) group:** Alkyl halides on reaction with hydrosulphide group forms thiols or mercaptans.

9) **Replacement by carboxylate group:** Alkyl halides on reaction with silver salts of carboxylic acid gives esters.

II. Dehydrohalogenation Reactions:

When haloalkanes are heated with alcoholic KOH, they undergo dehydrohalogenation to form alkenes. This is also known as α,β elimination reaction.

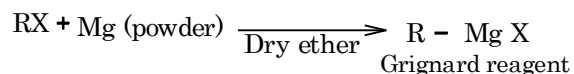
III. Reactions with Metals:

- 1) **Reaction with sodium.** This reaction is known as Wurtz reaction and generally used to prepare symmetrical alkanes with more number of carbon atoms.

Bromoethane undergoes Wurtz reaction to give butane.

2-chloropropane undergoes Wurtz reaction to give 2, 3 - dimethyl butane

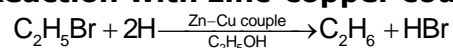
2) Reaction with magnesium.



IV. Reduction:

- 1) **Reaction with H₂ / Ni:** $\text{RX} + \text{H}_2 \xrightarrow[525 \text{ K}]{\text{Ni}} \text{R - H} + \text{HX}$

- 2) **Reaction with zinc-copper couple** (in presence of alcohol):



Similarly, Zn / HCl, Zn / NaOH, Na / C₂H₅OH, Sn / HCl or HI / red P at 430 K can also be used to reduce haloalkanes to alkanes.

- ⊙ TEL is tetraethyl lead which is added to petrol as an antiknocking agent

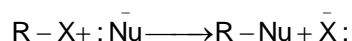
Saytzeff's rule:

During the elimination of hydrogen halides, the hydrogen atom must be removed from the carbon atom containing least number of hydrogen atoms.

Example:

Dehydrohalogenation of 2-bromobutane using alcoholic potash gives 2-butene (and not 1-butene) as major product as required by Saytzeff's rule.

Substitution reactions: The alkyl halides are highly reactive due to high electronegativity difference between carbon and halogen atom, which provides polarity in $\text{C}^{\delta+}-\text{X}^{\delta-}$ bond. Thus, carbon atom of C-X bond is easily attacked by a nucleophile and shows nucleophilic substitution.



The nucleophilic substitution may follow S_N1 or S_N2 mechanism.

S_N2 reactions are one-step reactions and occur through the intervention of a transition state. They are always accompanied by inversion of configuration also called Walden inversion. If the alkyl halide is optically active, the product is also optically active. However, the product may or may not have the same sign of optical rotation.

S_N1 reactions are two step reactions and occur through the intermediate formation of carbocations. Since carbocations are prone to rearrangements, therefore, during S_N1 reactions sometimes rearranged products are formed.

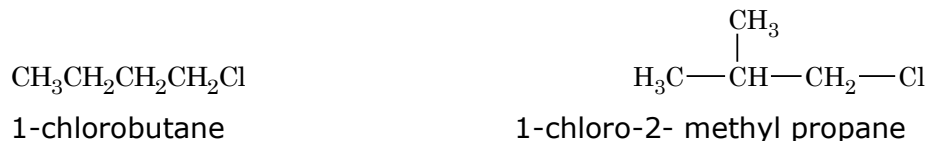
⊙ Characteristics and differences between S_N1 and S_N2 mechanism

S_N1 mechanism	S_N2 mechanism
1. Order of reactivity of Haloalkanes is $3^\circ > 2^\circ > 1^\circ$.	1. Order of reactivity of Haloalkanes is $1^\circ > 2^\circ > 3^\circ$.
2. Follows first order kinetics.	2. Follows second order kinetics.
3. Concentration of nucleophile can be low.	3. Concentration of nucleophile should be high.
4. Nucleophile can be mild in nature.	4. Nucleophile should be strong in nature.
5. Solvent should be of high polarity since ionization is required.	5. Solvent can be of low polarity. Since ionization is not required.
6. Nucleophile can attack from both the side. If the carbon of Haloalkane is asymmetric racemic mixture is formed.	6. Nucleophile attacks from the side opposite to halogen atom. If the carbon of Haloalkane is asymmetric the inversion configuration of an optical isomerism results.

Isomerism In Haloalkanes:

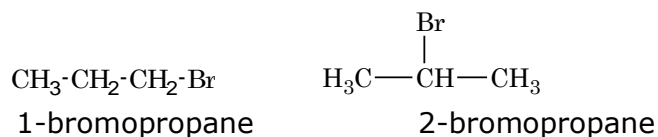
Chain Isomerism:

The haloalkanes having four or more carbon atoms show chain isomerism. For example,



Position Isomerism:

The haloalkanes with three or more carbon atoms show position isomersim. For example, $\text{C}_3\text{H}_7\text{Br}$ has two isomers.



(n-propyl bromide)

(iso-propyl bromide)

Preparation of arylhalides (haloarenes):

1) By Direct Halogenation:

The alkyl benzene when heated with halogens in the presence of sunlight and in the absence of Lewis acids (halogen carrier) undergoes substitution at the alkyl chain resulting in the formation of aralkyl halides.

2) From Diazonium Compounds:

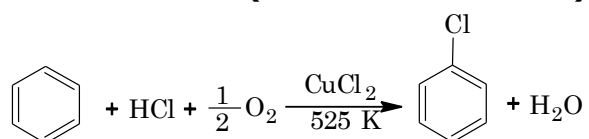
The diazonium compound is treated with CuCl and HCl or CuBr and HBr to give the corresponding haloarene. This reaction is known as Sandmeyer reaction.

If instead of CuCl and CuBr, Cu powder and HCl or HBr is used, the reaction is called Gattermann's reaction.

Iodoarenes are obtained by warming benzenediazonium salts with KI.

Fluoroarenes are obtained by the reaction of corresponding diazonium salts with fluoroboric acid to produce diazonium fluoroborate which on heating produces fluorobenzene. This reaction is called Balz-Schiemann reaction.

3) From Benzene (Commercial Method):



This process is known as Raschig process.

Physical Properties of Haloarenes

I. Melting and boiling point

1. For the same aryl group, the melting and boiling point decrease in the order: aryl iodide > aryl bromide > aryl chloride > aryl fluoride > benzene
2. For the same halogen atom, the melting and boiling point increases with the increase in molecular mass of the aryl halide.
3. In case of isomeric dihalobenzenes, the melting point of the p-isomer is higher than of o- and m-isomer.

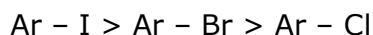
It is because p-isomer is more symmetrical. Their molecules are more closely packed in crystal lattice. The intermolecular forces of attraction in p-isomer are stronger and, therefore, its melting point is higher. The ortho and para isomers can be easily separated due to large difference in their melting points. The boiling point of isomeric dihalobenzenes are nearly same.

II. Solubility

Haloarenes are polar molecules. Even then they are insoluble in water. It is because they can not form hydrogen bond with water. They are soluble in organic solvents such as alcohol, ether, acetone, CHCl₃, CCl₄ etc.

III. Density

All aryl halides are heavier than water. For a given aryl group, density decreases in the order:



IV. Stability

For a given aryl group, the stability decreases in the order:

Order of stability: Ar-F > Ar-Cl > Ar-Br > Ar-I

Order of their reactivity is reverse to that of stability.

Order of reactivity: Ar-I > Ar-Br > Ar-Cl > Ar-F

It is because C-I bond length is largest in Ar-I. This bond can be broken up readily. C - F bond length is shortest and this bond is broken up with difficulty.

Explanation for low reactivity of aryl halides

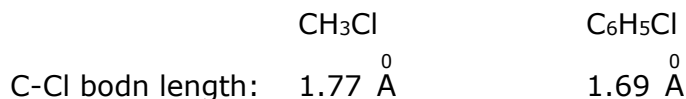
Both haloalkanes and haloarenes contain C-X bond. But haloarenes are less reactive than haloalkanes towards nucleophilic reagents. It can be explained by the following ways:

1. Resonance effect:

Aryl halides are stabilised by resonance. Therefore, activation energy for the replacement of halogen atom is higher for aryl halides. Due to greater activation energy, aryl halides are less reactive.

2. C-X bond length:

Secondly, due to resonance the C-Cl bond has double bond character. The C-Cl bond gets shortened. It is difficult to break a short bond. Thus, aryl halide is less reactive.



3. Energy of activation:

The energy of activation for displacement of halogen atom from aryl halides is greater than that of alkyl halides. Therefore, aryl halides are less reactive.

4. Different hybridisation state of carbon atom holding the halogen atom:

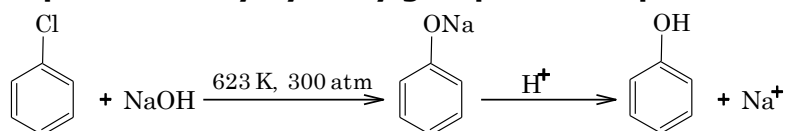
In CH₃-Cl and C₆H₅-Cl the carbon atom to which halogen atom is attached is in sp³ and sp² hybridisation state respectively. The sp² hybridised carbon is more electronegative and sp² hybridised orbital is smaller in size as compared to sp³ hybridised orbital. Therefore, this carbon atom in C₆H₅-Cl holds the shared electron pair of C-Cl bond more firmly. Hence, C-Cl bond in chlorobenzene gets shortened. It is difficult to break the C-Cl bond. It makes C₆H₅Cl less reactive.

5. Polarity of C-X bond:

Dipole moment of CH₃Cl and C₆H₅Cl is 1.94 D and 1.7 D respectively. Thus C-Cl bond in C₆H₅Cl is less polar. Smaller the polarity of a bond, greater is its bond strength. Hence, C₆H₅Cl is less reactive. Thus, it is difficult to break the C-Cl bond.

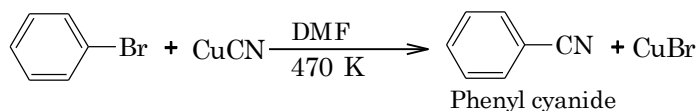
I. Nucleophilic Substitution Reactions:

1) Replacement by hydroxy group – Dow's process:

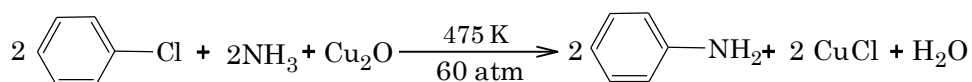


The reactivity of aryl halides towards nucleophilic substitution increases if some electron withdrawing group such as nitro, cyano or carbonyl group is attached to the ring.

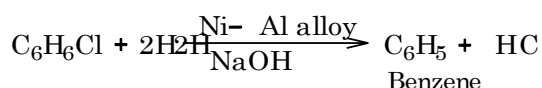
2) Replacement by cyano group:



3) Replacement by amino group.

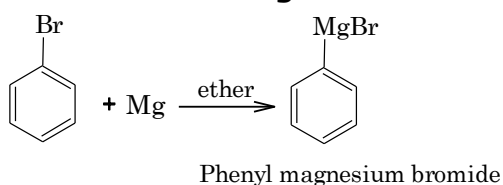


II. Reduction:

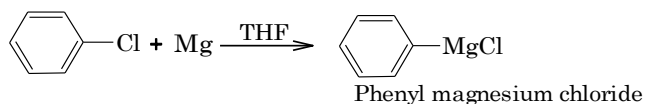


III. Reaction with Metals:

1) Reaction with magnesium:

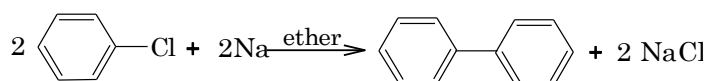


Aryl chlorides do not form Grignard reagent in presence of ether as solvent but it is possible if THF (Tetrahydrofuran) is used.

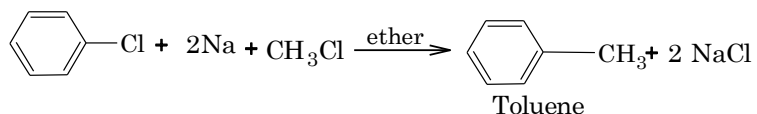


2) Reaction with sodium:

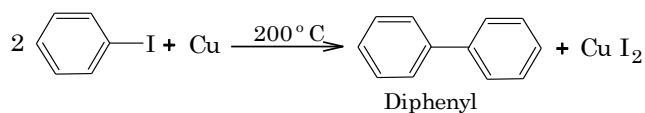
Aryl halides react with sodium in presence of ether.



When aryl halides are treated with haloalkane and sodium in presence of dry ether, undergo Wurtz Fitting reaction.



3) Reaction with copper powder (Ulmann Reaction):



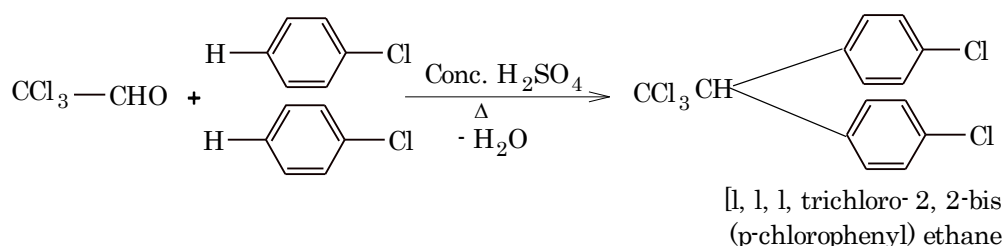
IV. Ring substitution reactions:

Aryl Halides undergo electrophilic substitution reaction in the benzene ring. The halogen atoms are o and p-directing groups but deactivates the ring at the same

time. Therefore, substitution occurs relatively at slower rate in comparison to benzene.

- 1) **Halogenation:** In the presence of halogen carrier ortho and para dichlorobenzene are formed
- 2) **Nitration:** ortho and para nitro chlorobenzene are formed
- 3) **Sulphonation:** ortho and para chloro benzenesulphonic acids are formed
- 4) **Friedel-Crafts alkylation:** ortho and para chloro toluene are formed
- 5) **Friedel-Crafts acylation:** Ortho and para chloro acetophenone are formed.
- 6) **Action with chloral:**

Two molecules of chlorobenzene reacts with (chloral) to form DDT.



Trichloromethane (Chloroform):

Methods of Preparation:

1. From methane:

Chloroform is prepared by chlorination of methane in the presence of light.

2. From chloral hydrate:

Chloroform (in pure form) can be prepared by distillation of chloral or chloral hydrate with concentrated aqueous NaOH solution or KOH solution.

3. From ethanol or acetone (lab method):

Chloroform is obtained from ethanol or acetone by reaction with a paste of bleaching powder and water.

4. From carbon tetrachloride:

By partial reduction of carbon tetrachloride with iron filings and water.

Physical Properties:

Chloroform is a colourless, heavy liquid. It has sweetish, sickly odour and taste. It is heavier than water and slightly soluble in water. Its boiling point is 334 K. Inhaling of chloroform causes unconsciousness and thus used as anaesthetic.

Chemical Properties:

1. Action of sunlight and air:

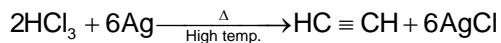
It is oxidized by air to produce a highly poisonous compound called phosgene (COCl_2).

To avoid the formation of phosgene, chloroform is kept in dark bottles to cut off active light radiations and filled upto brim to keep out air. Also a little amount of 1% ethanol is added which converts the toxic COCl_2 as non-poisonous diethyl carbonate.

2. Hydrolysis:

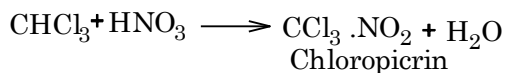
When boiled with aqueous KOH, chloroform is hydrolysed to potassium formate.

3. Action of Ag powder:



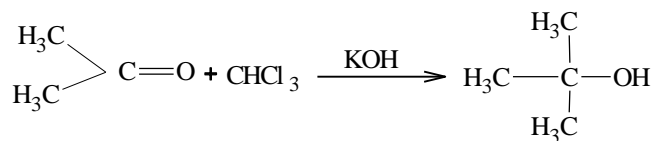
Acetylene

4. Reaction with nitric acid:



Chloropicrin is used as an insecticide and war gas.

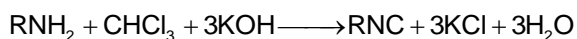
5. Reaction with acetone:



Chloretone

Chloretone is used as hypnotic (a sleep inducing drug).

6. Reaction with primary amines. (Carbylamine reaction):



Alkyl isocyanide

Uses of Chloroform:

- (i) As an anaesthetic.
- (ii) As laboratory reagent—detection of primary (1°) amines.
- (iii) As a solvent for fat, waxes, rubbers, varnishes.
- (iv) As a preservative for anatomical specimens.
- (v) In preparation of chloretone and nitrochloroform.

Triiodomethane (Iodoform):

Methods of Preparation:

Iodoform is prepared by the action of iodine and alkali on acetaldehyde, methyl ketones and alcohols

Physical Properties:

Iodoform is a yellow coloured, solid compound having melting point 382 K. It is insoluble in water but dissolves readily in organic solvents.

Uses of Iodoform:

- (i) It is used as antiseptic for dressing wounds.
- (ii) It is used for manufacturing pharmaceuticals.