

Haloalkanes and Haloarenes

Module 32.1: Nomenclature- nature of C-X bond, Physical and Chemical properties, S_N1 and S_N2 mechanism

Introduction:

The halogen derivatives of aliphatic hydrocarbons are called haloalkanes and halogen derivatives of aromatic hydrocarbons are called haloarenes. These are obtained when the hydrogen atom of an alkane or an arene is replaced by a halogen atom [F, Cl, Br or I]. The general formula is C_nH_{2n+1}X for haloalkanes and for haloarenes the general formula is Ar – X. **Haloalkane** is represented by RX, where R is an alkyl group. Monohalogen derivatives of alkanes are called haloalkanes or alkyl halides. **Haloarenes** is represented by ArX where Ar is aryl group and X is a halogen atom.

The halogen derivatives of hydrocarbons are classified on the basis of nature of hydrocarbon from which they are obtained as:

- (i) **Alkyl halides:** Halogen derivative of alkanes
- (ii) **Alkenyl halides:** Halogen derivative of alkenes (Not included in syllabus)
- (iii) **Alkynyl halides:** Halogen derivative of alkynes (Not included in syllabus)
- (iv) **Aryl halides:** Halogen derivative of arenes. (see aromatic part)

Alkyl halides are further classified as:

- (i) **Mono halides:** These involve replacement of one H atom by halogen atoms i.e., C_nH_{2n+1} X.

Ex:

CH₃Cl: methyl chloride or chloromethane

C₂H₅Cl: ethyl chloride or chloroethane

(ii) Di halides: These involve replacement of two H atoms by halogen atoms i.e., $C_nH_{2n}X_2$

CH_2X : methylene halide

$\begin{array}{c} CH_2X \\ | \\ CH_2X \end{array}$: ethylene dihalide or vicinal dihalides

$\begin{array}{c} CH_3 \\ | \\ CHX_2 \end{array}$: ethylidene dihalide or geminal dihalides

(iii) Tri halides: These involve replacement of three H atoms by halogen atoms i.e., $C_nH_{2n-1}X_3$

Ex: CHX_3 : trihalo methane or haloform

(iv) Tetra halide: These involve replacement of four H atoms by halogen atoms i.e., $C_nH_{2n-2}X_4$

Ex: CCl_4

Monohalides or Alkyl halides:

(1) General formula $C_nH_{2n+1}X$

Ex: CH_3X , C_2H_5X etc.,

(2) Mono halides are further classified as:

(A) Primary halides: Halogen atom attached on 1° carbon or methyl carbon

Ex: CH_3X : halomethane or methyl halide

CH_3CH_2X : haloethane or ethyl halide

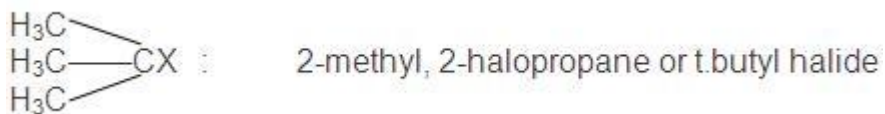
$CH_3CH_2CH_2X$: 1-halopropane or n-propyl halide

(B) Secondary halides: Halogen atoms are attached on 2° carbon atom

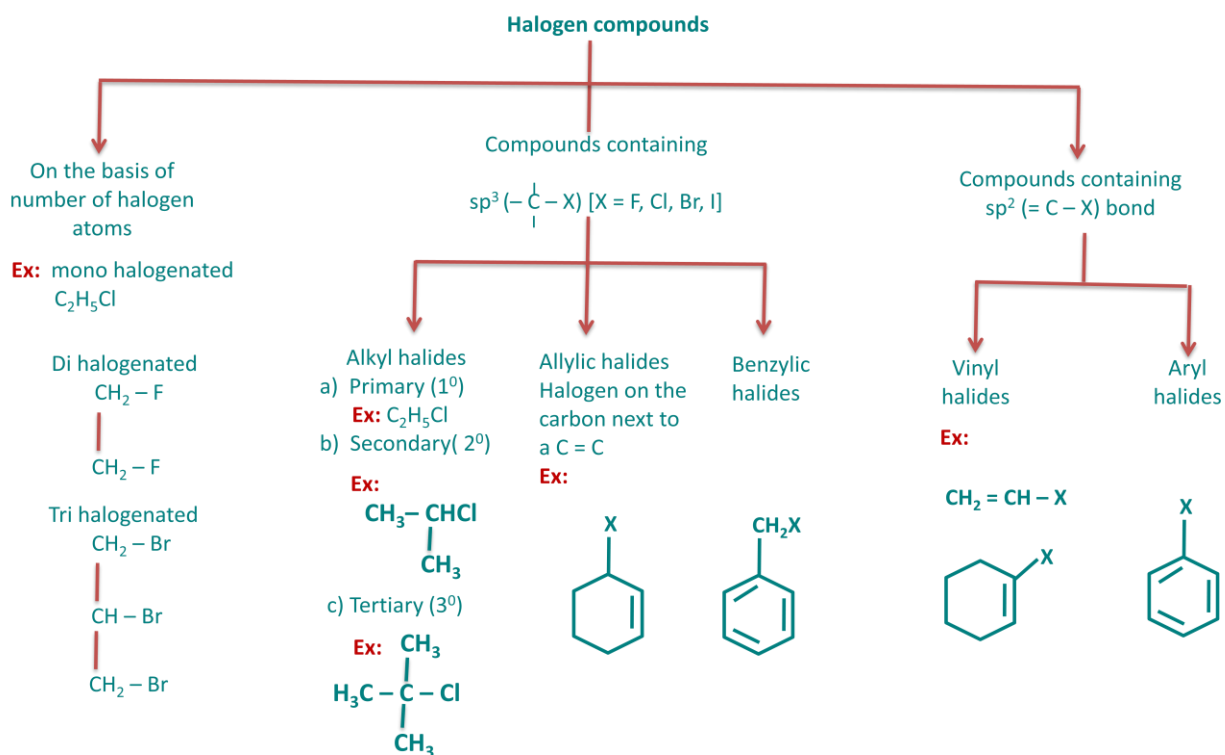
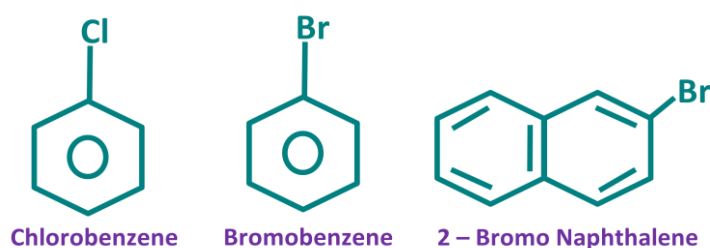
CH_3CHXCH_3 : 2-halopropane or sec. propyl halide or isopropyl halide

$\text{CH}_3\text{CHXCH}_2\text{CH}_3$: 2-halobutane or sec. butyl halide

(C) Tertiary halides : Halogen atoms are attached on 3° carbon atom



Aryl halides (haloarenes) are halogen derivatives of aromatic hydrocarbons, which are derived by replacing hydrogen atom attached to the aromatic ring by a halogen atom. Therefore, in haloarenes the halogen atom [F, Cl, Br or I] is directly attached to the aromatic ring. For example



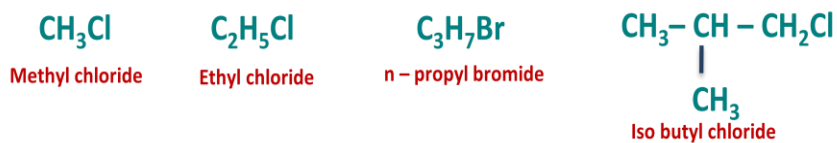
Nomenclature of mono haloalkanes and mono haloarenes:

Two methods are in use

1. Common or trivial system:

The monohalogen derivatives of alkanes are alkyl halides. Their names are written by naming the alkyl group attached to halogen first and then adding the word halide.

Example:

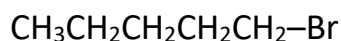


The names of the alkyl groups and the halides are written in two separate words. The prefixes n-, iso-, sec-, tert-, etc., are also used for alkyl groups to represent the type of carbon chain in the compound.

n – prefix:



n – Butyl chloride



n – Pentyl bromide

The prefix 'n-' is used for alkyl group having continuous chain of carbon atoms with no branching.

Iso - prefix:

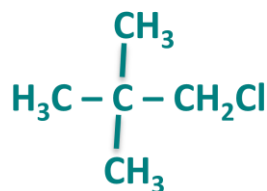


The prefix 'iso-' is used for those alkyl groups where one methyl group is attached to a carbon that is next to the end C-atom.

Neo – prefix:

The prefix ‘neo–’ is used for those alkyl groups which have two methyl groups attached to a carbon that is next to the end C–atom.

Example:

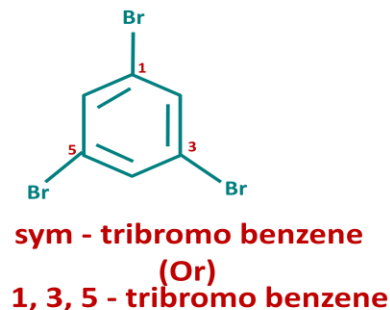


Neo – pentyl chloride

Aryl halides:

Aryl halides are named by adding the prefix ‘halo’ [fluoro, chloro, bromo iodo etc.] before the name of the aromatic hydrocarbon. In case of di – substituted compounds, the relative positions of the substituted groups, (1, 2); (1, 3); and (1, 4) are indicated by the prefix ortho (o -), meta (m -) and para (p -) respectively. When more than two substituents are present, their positions are indicated generally by numerical indices.

For example:



2. IUPAC System:

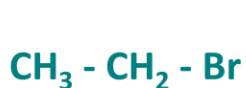
The mono halogen derivatives of alkanes are named as haloalkanes. While writing the names, the word 'halo' is prefixed to the name of the alkane corresponding to the longest continuous carbon chain that has the halogen atom. In case of branched chain alkanes, the following rules are followed.

The longest continuous chain containing the carbon that is attached to halogen group is selected as the parent alkane.

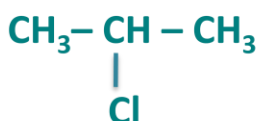
The carbon atom is numbered in a way that the carbon atom carrying the halogen atom gets the lowest number.

The positions of the halogen atom and the other alkyl groups are indicated by suitable numerical prefixes i.e. 1, 2, 3 etc. Other common rules of alkanes are followed.

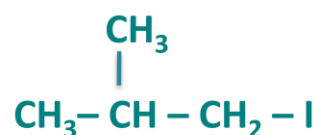
For example:



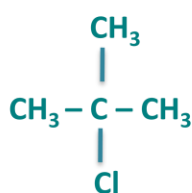
Bromoethane



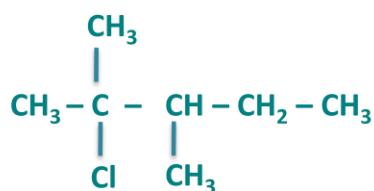
2 - Chloro propane



1 - Iodo, 2 - methyl propane



2 - Chloro, 2 - methyl propane



2 - Chloro, 2, 3 - dimethyl pentane

The common and the IUPAC names of a few alkyl halides are given below:

Alkyl halide	Common name (Alkyl group + halide)	IUPAC name (Prefix + halo + alkane)
CH_3Cl	Methyl chloride	Chloro methane
$\text{CH}_3 - \text{CH}_2 - \text{Br}$	Ethyl bromide	Bromo ethane
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{I}$	n – propyl iodide	1 – Iodo propane
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{I} \\ \\ \text{CH}_3 \end{array}$	Iso propyl iodide	2 – Iodo propane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	n – butyl chloride	1 – chloro butane
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{Cl} \\ \\ \text{CH}_3 \end{array}$	Iso – butyl chloride	1 – chloro, 2 – methyl propane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{Cl} \\ \\ \text{CH}_3 \end{array}$	Neo – pentyl chloride	1 – chloro, 2, 2 – di methyl propane

Nature of C – X bond:

Halogens are more electronegative elements than carbon. Due to the difference in the electronegativity values of carbon and halogen in alkyl halide, it shows polarity. The partial positive charge is on carbon atom and partial negative charge is present on halogen atom after polarisation.

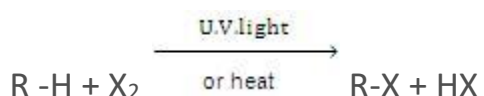


The size of halogen atom increases as we go down the group in the periodic table; fluorine atom is the smallest and iodine atom is the largest in the VIIA group. Consequently the carbon – halogen bond length also increases from C – F to C – I. As the bond length increases the bond enthalpy decreases.

Bond	Bond length (in pm)	Bond enthalpies (in kJ mol ⁻¹)
CH ₃ – F	139	452
CH ₃ – Cl	178	351
CH ₃ – Br	193	293
CH ₃ – I	214	234

Preparation methods of Monohalides:

(1) By direct halogenations of alkanes: (See halogenations of alkanes)

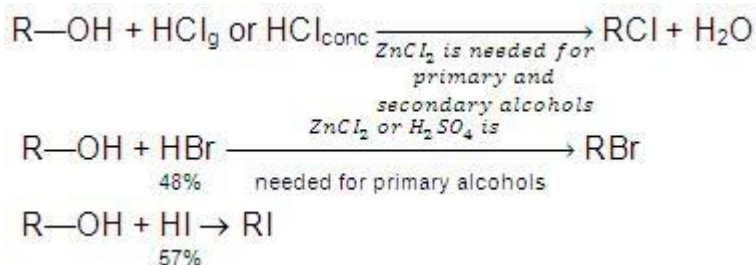


(2) By the addition of HX on alkenes:



(3) By alcohols:

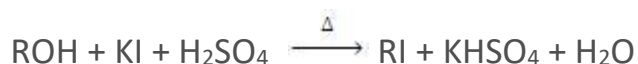
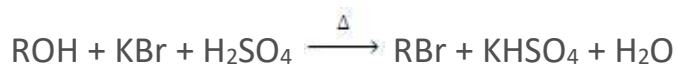
(a) Action of halogen acids:



The reactivity order for alcohols is: tertiary > secondary > primary alcohol

The reactivity order for halogen acid is: HI > HBr > HCl

Note: Bromides and iodides are also obtained by the following:

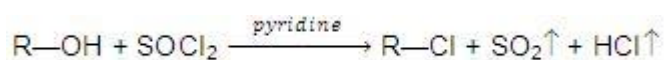


(b) Action of phosphorus halides:



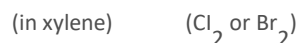
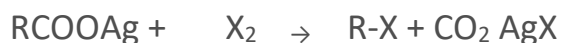
Note : PBr_3 & PI_3 being less stable & thus for bromides & iodides, $\text{P} + \text{Br}_2$ or $\text{P} + \text{I}_2$ mixture is used.

(c) Action of thionyl chloride: or Darzen's method:



Note : SOBr_2 is less stable & SOI_2 does not exist and thus bromides & iodides are prepared by this method.

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



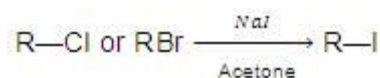
Note :

1. The yield of alkyl halide is primary > secondary > tertiary
2. Hunsdiecker reaction is used to reduce the length of carbon chain (descent of series).
3. Only bromides are obtained in good yield in this reaction. The chlorides can also be obtained by this reaction but the yield is poor. Iodides however cannot be obtained because these form esters with silver salts.

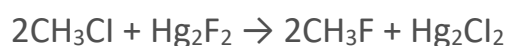


This reaction is called Birnbaum-Simonini reaction.

5. By halide exchange: Iodides are usually prepared by this method. The halogen exchange reaction is called Finkelstein reaction.



This method is also used to prepare fluorides.



Physical properties:

Alkyl halides are colorless when pure. However bromides and iodides get color on standing or on exposure to light. They have pleasant odour. Many volatile halogen compounds have sweet smell. Lower alkyl halides are gases but higher alkyl halides are either liquids or solids. Alkyl halides are more polar and have higher molecular masses when compared to the parent hydrocarbons. Because of these two reasons they have stronger inter molecular forces of attraction and possess high boiling points and melting points compared to parent hydrocarbons. For a given R, the order of melting points and boiling points would be $\text{RI} > \text{RBr} > \text{RCI} > \text{RF}$. Among isomeric alkyl halides the boiling points decrease with increase in branching. As the branching increases the adjacent molecules are not able to come close to be attached strongly. For butyl bromide $\text{C}_4\text{H}_9\text{Br}$ we have the following structures and the corresponding boiling points are shown.

Compound Structures	Name	Boiling point (K)
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \text{ Br}$	n – butyl bromide	375
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ \\ \text{Br} \end{array}$	2 – bromo butane	364
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C} - \text{C} - \text{CH}_3 \\ \\ \text{Br} \end{array}$	2 – bromo, 2 – methyl propane	346

The density of these compounds increases with increase in number of carbon atoms in the chain, the number of halogen atoms and the atomic masses of halogen atoms.

Compound	Density (g ml ⁻¹)	Compound	Density (g ml ⁻¹)
n – C ₃ H ₇ Cl	0.89	CH ₂ Cl ₂	1.336
n – C ₃ H ₇ Br	1.335	CHCl ₃	1.489
n – C ₃ H ₇ I	1.747	CCl ₄	1.595

The halogen compounds are only slightly soluble in water. In order to make a haloalkane dissolve in water, energy is required to overcome the intermolecular 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; 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.

Chemical nature of Alkyl halides:

(a) The alkyl halides are highly reactive due to the high electronegativity difference between carbon & 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 to show nucleophilic substitution.



The nucleophilic substitution may follow S_N1 or S_N2 mechanism. In addition to nucleophilic substitution alkyl halides also show elimination reactions.

(b) Furthermore the reactivity order of alkyl halide is:



The reactivity does not follow the polarity order of bond. On the contrary it has been explained in terms of increasing bond length of C-X bond (maximum in C-I) which gives rise to lower bond energy and thus less stability to C-X bond.

(c) The reactivity orders for given alkyl halide also shows the order:

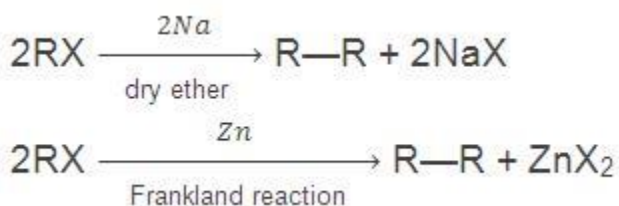


This has been explained in terms of +ve inductive effect of alkyl groups which increases the polarity of C-X bond & thereby making it more reactive.

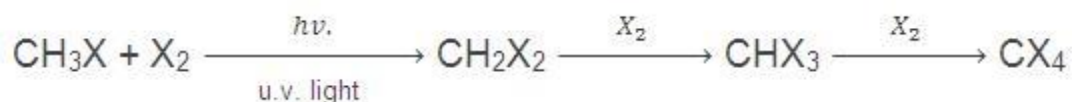
(d) Primary alkyl halides undergo reactions by S_N2 mechanism. The presence of bulky groups in primary halides (inspite of more +ve I.E.) cause steric hindrance & bring them less reactive towards.



1. Wurtz reaction:

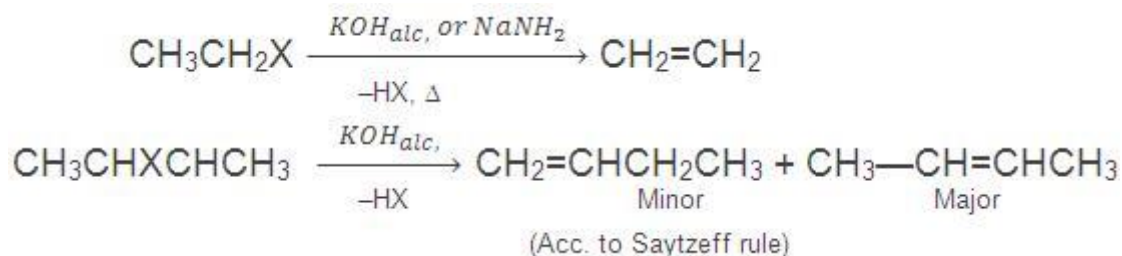


2. Action of halogen:



Note: C_2Cl_6 (hexachloroethane) is a solid and is known as artificial camphor.

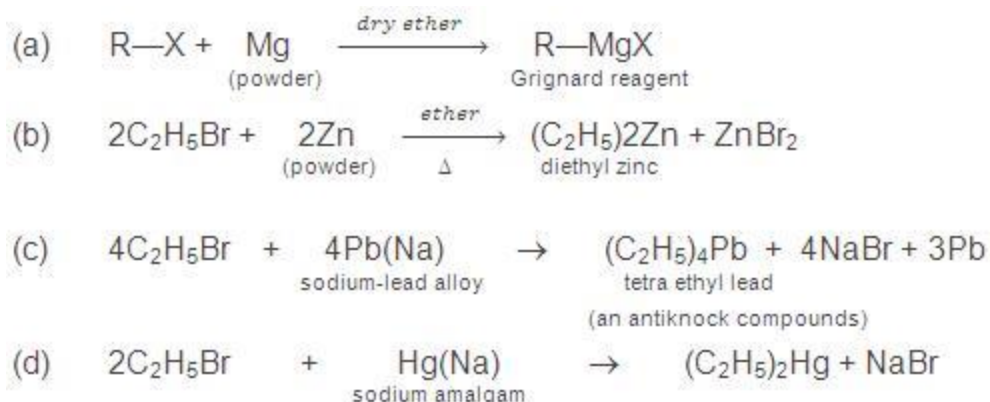
3. Dehydrohalogenation : An α, β -elimination of HX by KOH_{alc} .



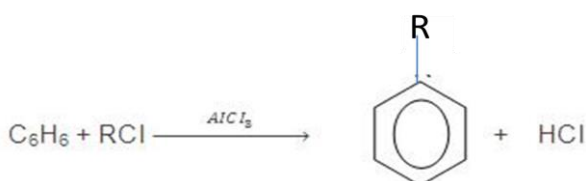
4. Action of heat : $RCH_2CH_2X \xrightarrow{300^\circ C} RCH=CH_2 + HX$

5. Reduction: $R-X + 2H \xrightarrow{\text{Reducing agent}} R-H + HX$

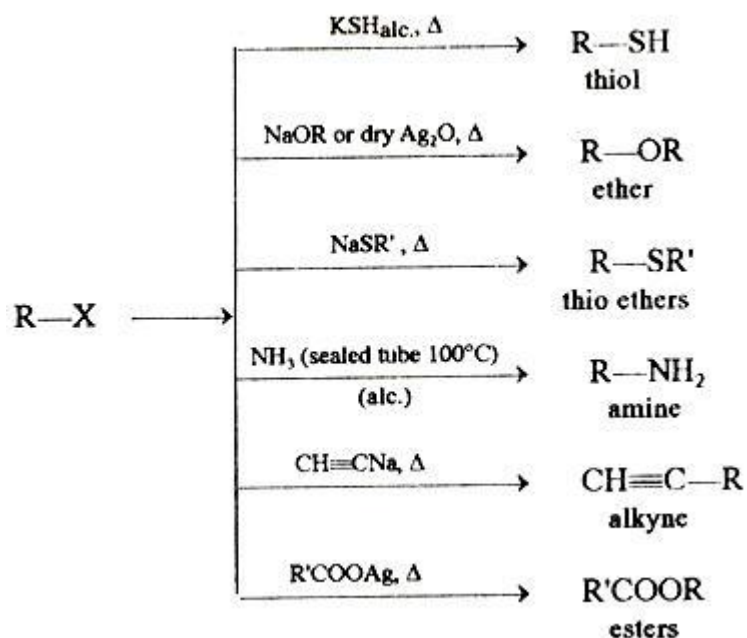
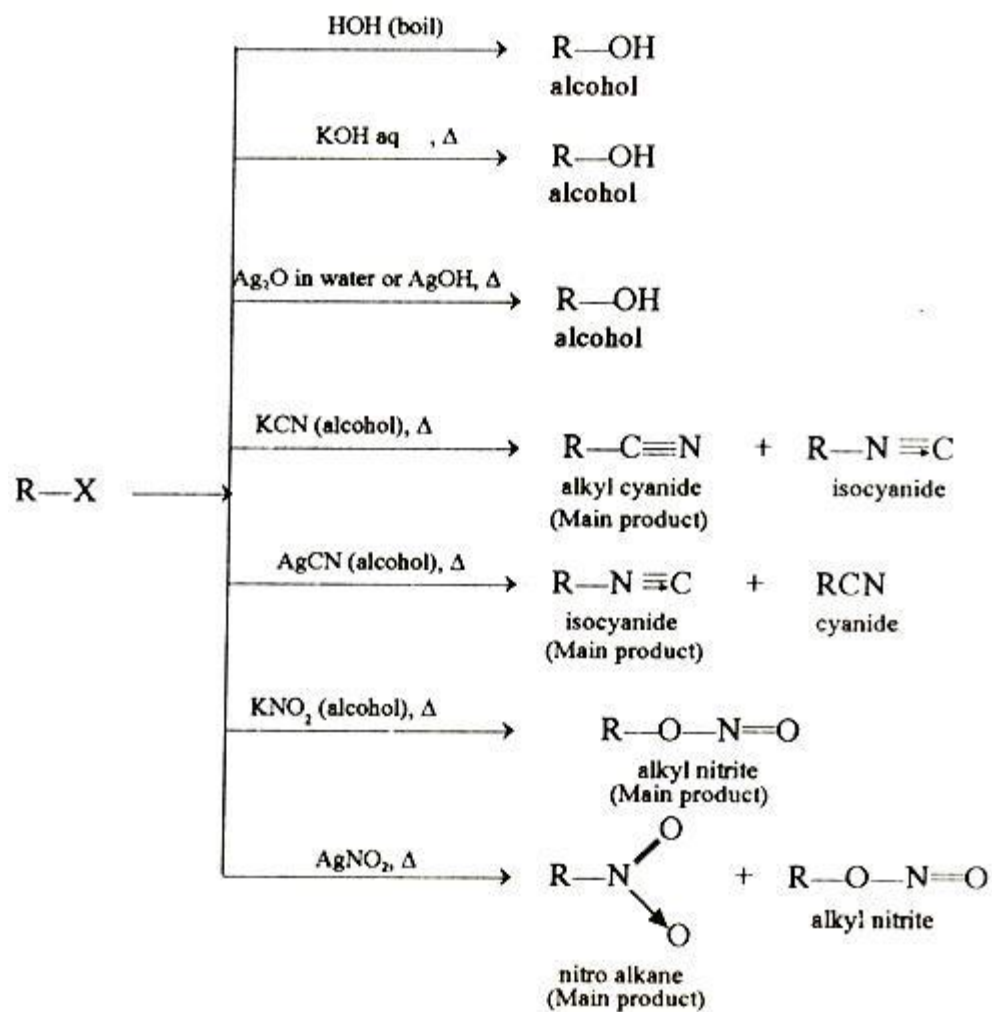
6. Reactions with metals:



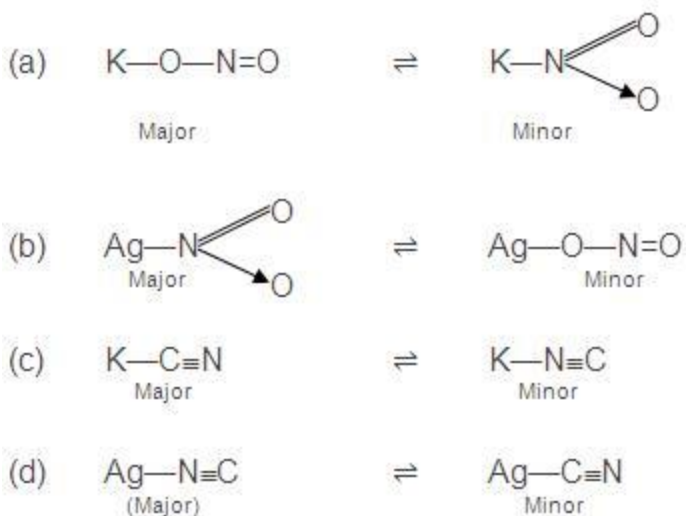
7. Friedel-Craft's reaction: Alkyl halides react with benzene in presence of anhydrous $AlCl_3$ to form homologues of C_6H_6 .



8. Nucleophilic substitution on alkyl halides: Halogen atom of alkyl halides is easily replaced by other nucleophiles to give a large variety of S_N reactions.



Note: The two products formed on reaction of R-X with KNO_2 and AgNO_2 as well as with KCN and AgCN are due to tautomerism in these molecules.

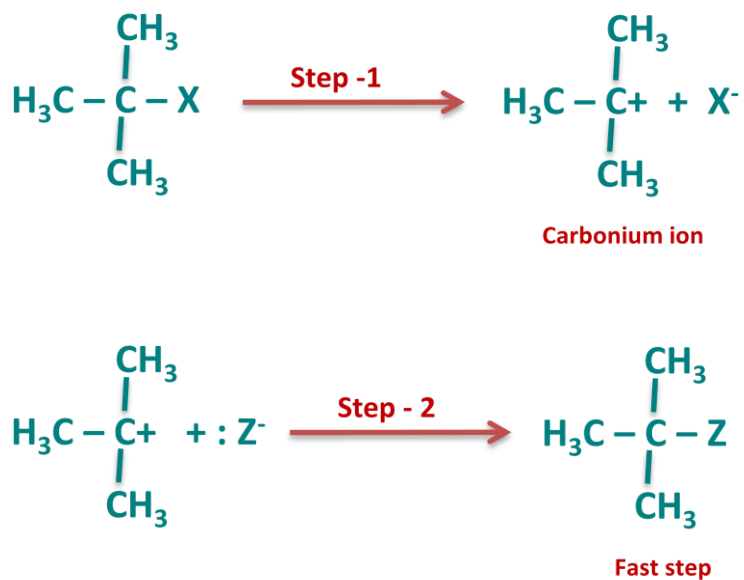


Types of nucleophilic substitution reactions:

The nucleophilic substitution reactions can be classified into two types.

S_N^1 reaction mechanism [studied as substitution nucleophilic, first order reaction]:

This type of reaction proceeds in two steps as:



The first step is slow and is the rate – determining step. As the nucleophile (Z^-) is not involved in the rate - determining step, the reaction depends only upon the concentration of alkyl halide (RX) and is therefore, a first order reaction.

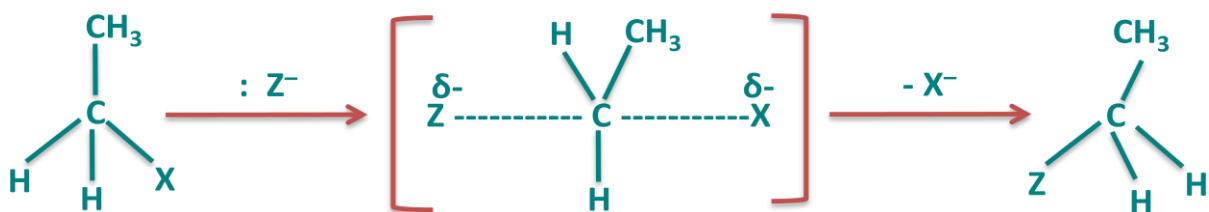
$$\text{i.e. Rate} = K [RX]$$

The order of reactivity depends upon the stability of carbonium ion formed in the first step. Since the 3° carbonium ion is most stable, the ionization of tertiary alkyl halide is favoured. The order of reactivity for S_N1 reaction is

Tertiary > secondary > primary

S_N2 reaction mechanism [studied as substitution nucleophilic, second order reaction]:

This type of reaction occurs in one step through the formation of transition state as:



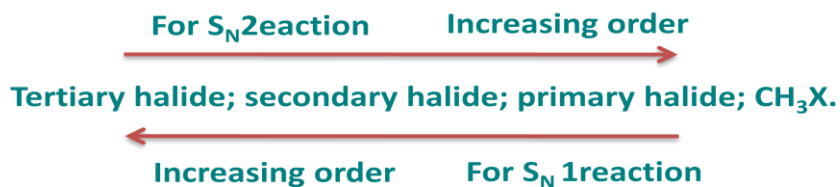
Here, the rate of reaction depends upon the concentration of both the alkyl halide and the nucleophile.

$$\text{i.e. Rate} = K [RX] [Z^-]$$

The transition state form of tertiary alkyl halide is less stable due to steric hindrance. i.e. crowding of alkyl groups. The order of reactivity is

Primary > Secondary > Tertiary

Thus the reactivity of S_N1 versus S_N2 is:



Uses:

- (i) As alkylating agent i.e., to introduce alkyl group in a molecule.
- (ii) Lower members are used as anaesthetic agent, refrigerant and solvents.
- (iii) As synthetic reagent.

Assignment questions:

1. Explain the classification of haloalkanes
2. Give a brief account on the nomenclature of haloalkanes.
3. Discuss the mechanisms of nucleophilic substitution reactions in alkyl halides
4. Write the methods preparation and properties of alkyl halides.
5. Arrange the following in the increasing order of their boiling points.
 - i. Bromo methane; bromoform; chloromethane;
 - ii. n – Propyl chloride; isopropyl chloride; n – Butyl chloride

Give your explanation.

SAQs:

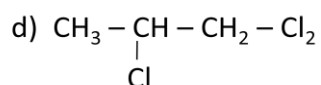
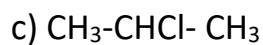
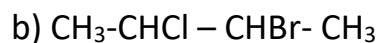
1. The alkyl halide among the following
 - a. $C_nH_{2n+1}X$
 - b. $C_nH_{2n-1}X$
 - c. $C_nH_{2n}X$
 - d. $C_nH_{(2n-2)}X$

Solution: a)

2. Identify a secondary alkyl halide from the following.
 - a. $(CH_3)_3CCH_2Br$
 - b. $(CH_3)_3CBr$
 - c. $(CH_3)_2CHCl$
 - d. $CH_3(CH_2)_3CH_2I$

Solution: c)

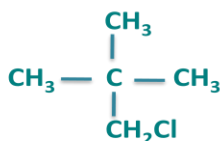
3. Which of the following is isopropyl chloride?



Solution: c)

4.

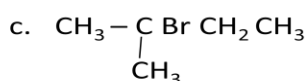
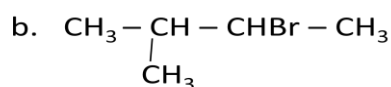
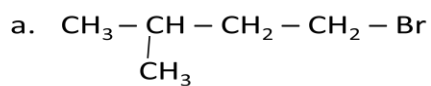
The IUPAC name of

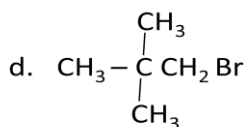


- a. 1 – chloro, 2 – methyl pentane
- b. 2, 2 – di methyl, 3 – chloro propane
- c. 1 – chloro, 2, 2 – di methyl propane
- d. 1 – chloro, 2 – methyl isobutane

Solution: c)

5. The correct structure of 2 – bromo, 3 – methyl butane is





Solution: b)

6. The C – X bond in an alkyl halide is
- an ionic bond
 - a polar covalent bond
 - a non – polar covalent bond
 - a coordinate covalent bond

Solution: b)

LAQs:

1. Explain the nature of C – X bond.

Solution:

Nature of C – X bond:

Halogens are more electronegative elements than carbon. Due to the difference in the electron negativity values the carbon – halogen bond of an alkyl halide is polarized. The partial positive charge is on carbon atom and partial negative charge is present on halogen atom.



The size of halogen atom increases as we go down the group in the periodic table; fluorine atom is the smallest and iodine atom is the largest in the VII group. Consequently the carbon – halogen bond length also increases from C – F to C – I. As the bond length increases the bond enthalpy decreases.

Bond	Bond length (in pm)	Bond enthalpies (in kJ mol ⁻¹)
CH ₃ – F	139	452

$\text{CH}_3 - \text{Cl}$	178	351
$\text{CH}_3 - \text{Br}$	193	293
$\text{CH}_3 - \text{I}$	214	234

2. Discuss the physical properties of haloalkanes

Solution:

Physical properties:

Alkyl halides are colorless but bromides and iodides get color on standing or on exposure to light. They have pleasant odour. Lower alkyl halides are gases but higher alkyl halides are either liquids or solids. Alkyl halides are more polar and have higher molecular masses when compared to the parent hydrocarbons. Because of these two reasons they have stronger inter molecular forces of attraction and possess high boiling points and melting points compared to parent hydrocarbons. For a given R, the order of melting points and boiling points would be $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$. Among isomeric alkyl halides the boiling points decrease with increase in branching. As the branching increases the adjacent molecules are not able to come close to be attached strongly. For $\text{C}_4\text{H}_9\text{Br}$ we have the following structures and the corresponding boiling points are shown.

Compound Structures	Name	Boiling point (K)
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2\text{Br}$	n – butyl bromide	375
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ \\ \text{Br} \end{array}$	2 – bromo butane	364
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C} - \text{C} - \text{CH}_3 \\ \\ \text{Br} \end{array}$	2 – bromo, 2 – methyl propane	346

The density of these compounds increases with increase in number of carbon atoms in the chain, the number of halogen atoms and the atomic masses of halogen atoms.

Compound	Density (g ml ⁻¹)	Compound	Density (g ml ⁻¹)
n – C ₃ H ₇ Cl	0.89	CH ₂ Cl ₂	1.336
n – C ₃ H ₇ Br	1.335	CHCl ₃	1.489
n – C ₃ H ₇ I	1.747	CCl ₄	1.595

The halogen compounds are only slightly soluble in water. In order for a haloalkane to dissolve in water, energy is required to overcome the intermolecular 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; 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.

Problem set:

- The correct order of density in the following sets of compounds.
 - CH₃Cl > CH₂Cl₂ > CHCl₃ > CCl₄
 - CH₃Cl < CH₂Cl₂ < CHCl₃ < CCl₄
 - CH₃Cl > CCl₄ > CHCl₃ > CH₂Cl₂
 - CH₃Cl > CCl₄ > CH₂Cl₂ > CHCl₃

Solution: b)

- Which of the following alkylhalides is preferentially hydrolyzed by S_N¹ mechanism?
 - CH₃Cl
 - C₂H₅Cl
 - n -C₃H₇Cl
 - (CH₃)₃CCl

Solution: d)

- The order of reactivity of alkyl halides towards nucleophilic substitution is;

- a. $RI > RBr > RCl > RF$
- b. $RI < RBr < RCl < RF$
- c. $RI > RBr > RCl > RF$
- d. $RI < RBr > RCl < RF$

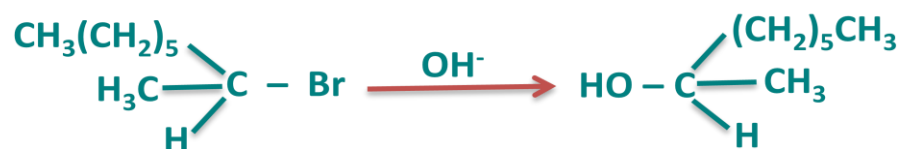
Solution: a)

4. The reaction $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$, follows _____ mechanism:

- a. S_N1
- b. S_N2
- c. S_E1
- d. S_E2

Solution: b)

5. The reaction described below is:



- a. S_E1
- b. S_N2
- c. S_N1
- d. S_E2

Solution: b)

6. Pick up the correct statement about alkyl halides: they

- a. have H – bonding
- b. are soluble in water
- c. do not behave as solvents
- d. do not contain any polar bond.

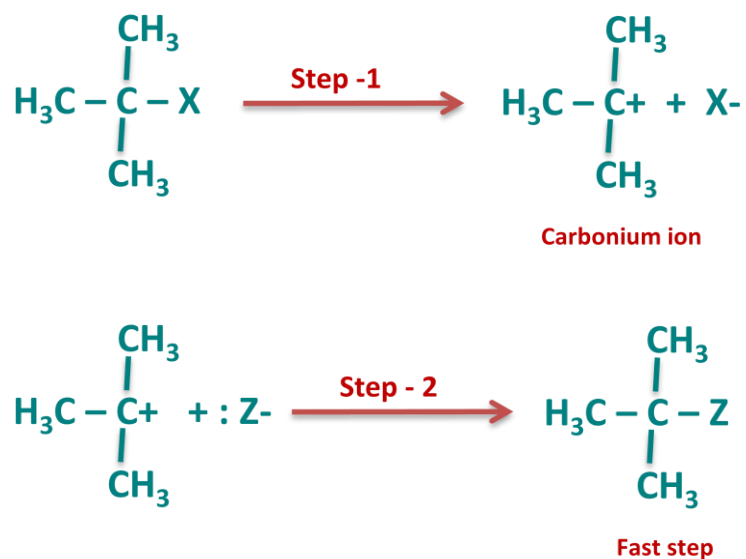
Solution: c)

7. Write the mechanism of S_N1 reaction of alkyl halides

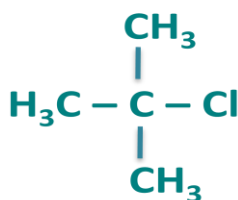
Solution:

S_N1 reaction [studied as substitution nucleophilic, first order reaction]:

This type of reaction proceeds in two steps as:



8. Write the common name and IUPAC name of the following compound.



Solution:

t – butyl chloride => common name.

2- chloro – 2 – methylpropane => IUPAC name.

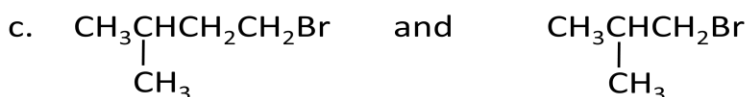
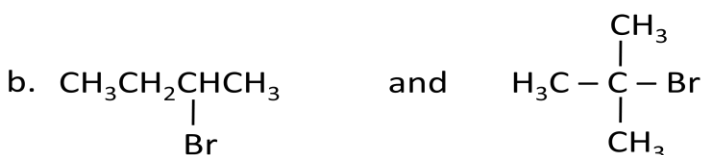
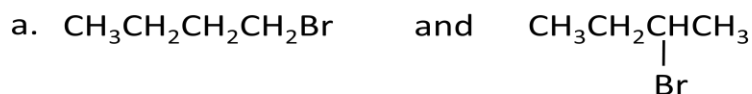
Exercise questions:

1. Write structures of the following compounds:

- 2-Chloro-3-methylpentane
- 1-Chloro-4-ethylcyclohexane

- c. 4-tert. Butyl-3-iodoheptane
- d. 1,4-Dibromobut-2-ene
- e. 1-Bromo-4-sec. butyl-2-methylbenzene

2. Write structures of different dihalogen derivatives of propane.
3. Which of the following pairs would you expect to react by an S_N2 mechanism? Explain your answer.

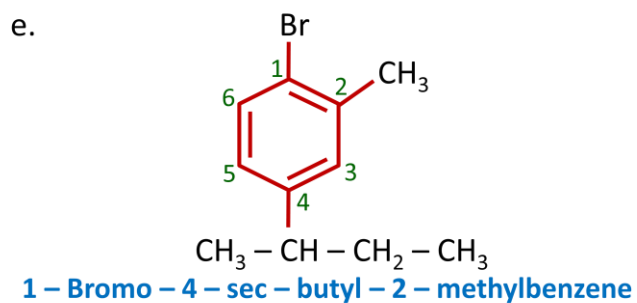
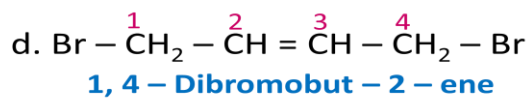
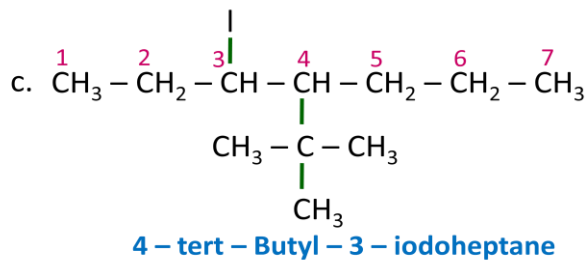
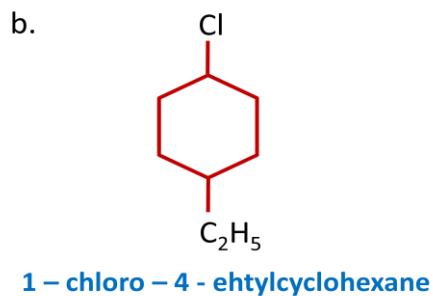
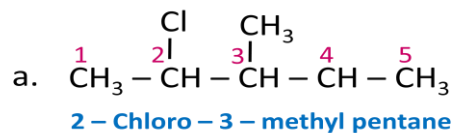


4. Which one of the following has the highest dipole moment?
 - a. CH_2Cl_2
 - b. CHCl_3
 - c. CCl_4
5. Which compound in each of the following pairs will react faster in S_N2 reaction with OH^- ?
 - a. CH_3Br or CH_3I
 - b. $(\text{CH}_3)_3\text{CCl}$ or CH_3Cl
6. Arrange the compounds of each set in order of reactivity towards S_N2 displacement:

3 – Bromo – 2 – methylbutane, 1 – Bromopentane, 2 – Bromopentane
7. Write down the preparation methods of alkyl halides
8. Discuss the chemical properties of alkyl halides.

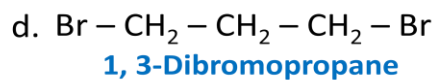
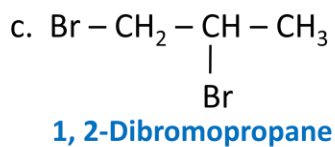
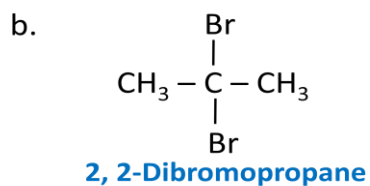
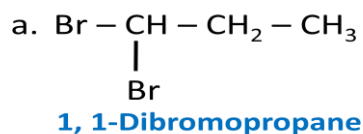
Solutions:

1.



2.

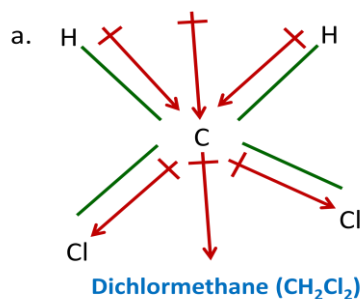
There are four different dihalogen derivatives of propane. The structures of these derivatives are shown below.



3.

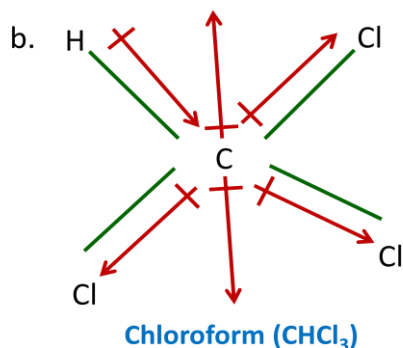
In option c) both the alkyl halides are 1° – alkyl halides. We know 1° – alkyl halides follow $\text{S}_\text{N}2$ mechanism.

4.



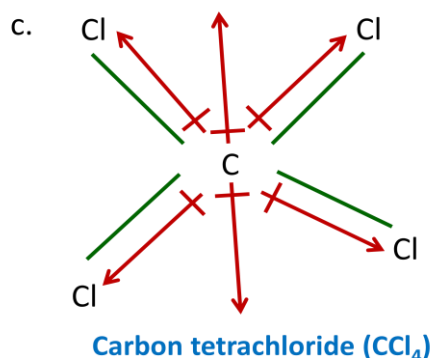
$$\mu = 1.60\text{D}$$

In case of CH_2Cl_2 , the resultant of the dipole moments of two C–Cl bonds is strengthened by the resultant of the dipole moments of two C–H bonds. As a result, CH_2Cl_2 has a higher dipole moment of 1.60 D than CHCl_3 i.e., CH_2Cl_2 has the highest dipole moment.



$$\mu = 1.08\text{D}$$

In CHCl_3 , the resultant of dipole moments of two C–Cl bonds is opposed by the resultant of dipole moments of one C–H bond and one C–Cl bond. Since the resultant of one C–H bond and one C–Cl bond dipole moments is smaller than two C–Cl bonds, the opposition is to a small extent. As a result, CHCl_3 has a small dipole moment of 1.08 D.



$$\mu = 0\text{D}$$

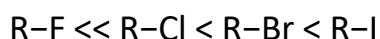
CCl_4 is a symmetrical molecule. Therefore, the dipole moments of all four C–Cl bonds cancel each other. Hence, its resultant dipole moment is zero.

Hence, the given compounds can be arranged in the increasing order of their dipole moments as:



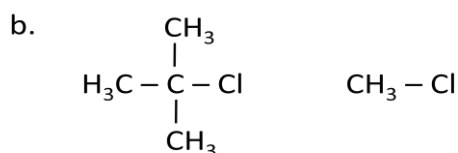
5.

- b. In the $\text{S}_{\text{N}}2$ mechanism, the reactivity of halides for the same alkyl group increases in the order.



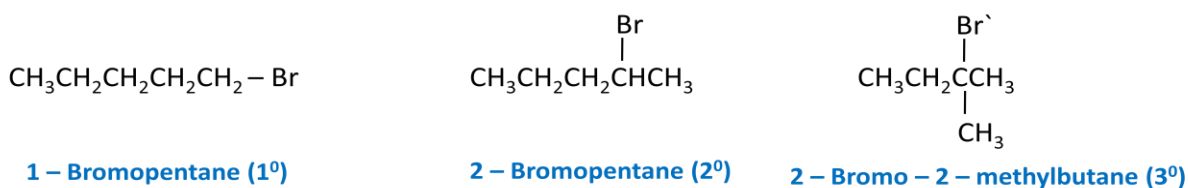
This happens because as the size increases, the halide ion becomes a better leaving group.

Therefore, CH_3I will react faster than CH_3Br in $\text{S}_{\text{N}}2$ reactions with OH^- .



The $\text{S}_{\text{N}}2$ mechanism involves the attack of the nucleophile at the atom bearing the leaving group. But, in case of $(\text{CH}_3)_3\text{CCl}$, the attack of the nucleophile at the carbon atom is hindered because of the presence of bulky substituents on that carbon atom bearing the leaving group. On the other hand, there are no bulky substituents on the carbon atom bearing the leaving group in CH_3Cl . Hence, CH_3Cl reacts faster than $(\text{CH}_3)_3\text{CCl}$ in $\text{S}_{\text{N}}2$ reaction with OH^- .

6.



An $\text{S}_{\text{N}}2$ reaction involves the approaching of the nucleophile to the carbon atom to which the leaving group is attached. When the nucleophile is sterically hindered, then the reactivity towards $\text{S}_{\text{N}}2$ displacement decreases. Due to the presence of substituents, hindrance to the approaching nucleophile increases in the following order.

1 – Bromopentane < 2 – bromopentane < 2 – Bromo – 2 – methylbutane

Hence, the increasing order of reactivity towards S_N^2 displacement is:

2 – Bromo – 2 – methylbutane < 2 – Bromopentane < 1 – Bromopentane

Haloalkanes and Haloarenes

Module 32.2: Ethyl chloride-preparation, properties & uses

Ethyl chloride, $\text{C}_2\text{H}_5\text{Cl}$, is a common name. It is also known by its IUPAC name as chloroethane.

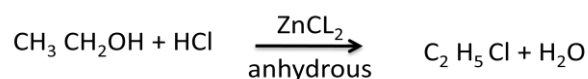
Preparation of ethyl chloride:

a. From alcohols:

This is the most widely used method for the preparation of haloalkanes. Here, the hydroxyl group ($-\text{OH}$) of the alcohol is replaced by the halogen atom (X).

i. Groove's process:

Primary alcohols produce chloroalkanes when hydrochloric acid vapours are passed through alcohol in the presence of anhydrous zinc chloride.

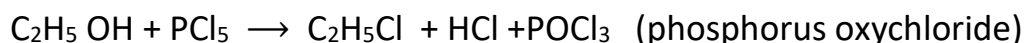
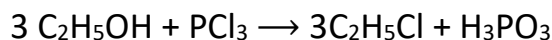


Pyridine, dimethyl amine and conc. Sulphuric acid are also used as catalyst for the above reaction.

ZnCl_2 , is a Lewis acid it readily coordinates with the oxygen atom of the alcohols. As a result, the $\text{C}-\text{O}$ bond weakens and breaks to form Carbocation. This reacts with chloride ion to form chloroalkanes. Thus, anhydrous ZnCl_2 helps in the cleavage of the $\text{C}-\text{O}$ bond.

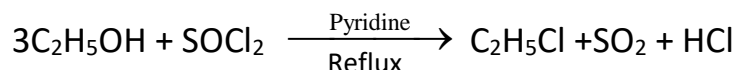
ii. By the action of phosphorus halides

Chloroalkanes can be prepared by the action of phosphorus penta chloride $[\text{PCl}_5]$ or phosphorus trichloride $[\text{PCl}_3]$ on the corresponding alcohols. For example ethyl chloride is prepared from ethyl alcohol.



iii. By the action of thionyl chloride (SOCl_2)

Chloroalkanes can also be prepared from alcohols by refluxing the alcohols with thionyl chloride in the presence of pyridine.



Similarly, Bromoalkanes, Iodoalkanes are obtained by heating alcohols with HBr or HI. These are produced by the action of phosphoric acid on potassium bromide or potassium iodide respectively.

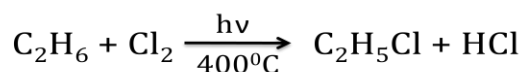
The order of reactivity of halogen acids on alcohols, in accordance with the bond dissociation energies of H-X bonds; is



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

b. Ethyl chloride from ethane:

Ethane reacts with Cl_2 at ordinary temperature in the presence of light to form ethyl chloride. In this reaction one or more hydrogen atoms may be substituted by chloride ion. $\text{C}_2\text{H}_5\text{Cl}$ is separated from the mixture.



c. From alkenes:

Haloalkanes can be prepared by the addition of halogen acids (HBr, HCl, HI) to alkenes in the presence of anhydrous aluminium chloride as catalyst.



Properties of ethyl chloride:

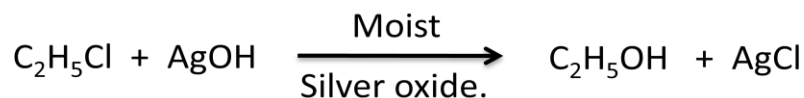
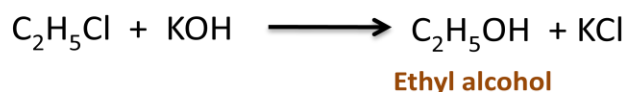
Physical properties:

It is a colourless gas with a pleasant odour. Its boiling point is 286K, and its density is 0.91 g/ml. It is soluble in organic solvents like carbon tetrachloride, but almost insoluble in water. As C – Cl bond is covalent it does not give Cl⁻ ions in solution. Hence it does not form a precipitate with silver nitrate solution.

Chemical properties:

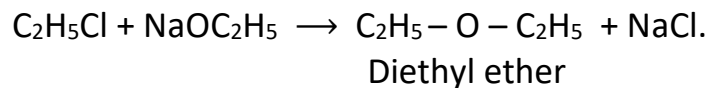
a. Replacement by hydroxyl group [Formation of alcohols]

On treatment with aqueous solution of KOH or moist silver oxide [Ag₂O/H₂O] chloro ethane gives alcohol. For example



b. Replacement by alkoxy group:

Ethyl chloride reacts with sodium ethoxide to form a diethylether. This is called Williamson's synthesis of ether. Similarly any other alkyl halide, on treatment with sodium alkoxide, undergoes with amson's reaction.

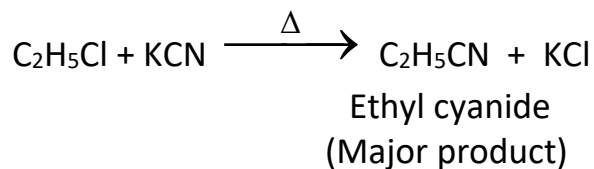


c. Substitution by cyanide and isocyanide group:

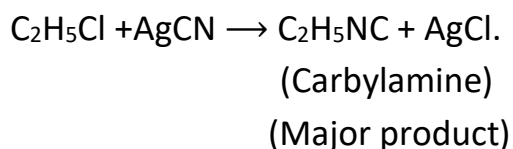
Haloalkanes react with an alcoholic solution of potassium cyanide to give alkylcyanides as the major products along with small amounts of alkyl isocyanides.

Example:

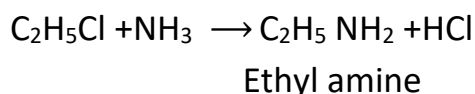
Ethyl chloride gives ethyl cyanide with KCN.



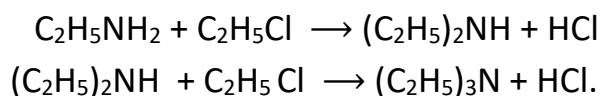
Isocyanides are obtained when haloalkanes are treated with alcoholic silver cyanide (AgCN). These are called carbylamines and have extremely unpleasant smell.

Example:**d. Substitution by amino group [Formation of amines]:**

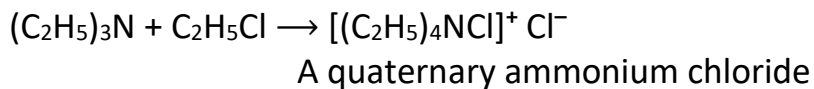
A primary amine is formed when a haloalkane is heated with alcoholic ammonia solution in a sealed tube at 383K; the halogen is substituted by -NH_2 group.



However, when haloalkane is in excess, a mixture of primary, secondary and tertiary amines is formed, as one or both the hydrogen atoms of the amino alkane produced [Primary amine] can be substituted by alkyl groups.

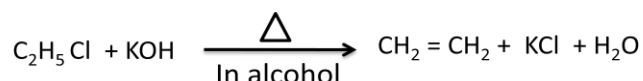


The tertiary amines which result, can also form quaternary ammonium salt by combining with another molecule of alkylhalide.



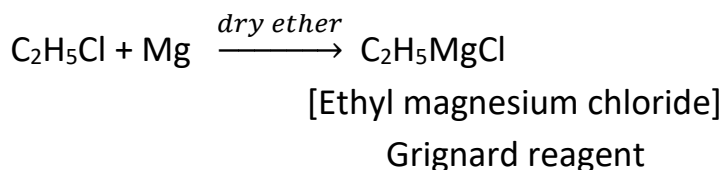
e. Elimination reactions (Dehydrohalogenation):

Haloalkanes undergo elimination of hydrogen halide (HX) when boiled with alcoholic solution of potassium hydroxide, (KOH alc) resulting in the formation of alkenes.



f. Action with magnesium [formation of Grignard reagent]:

When a solution of an alkyl halide, in dry ether, is treated with magnesium metal, an alkyl magnesium halide is formed.

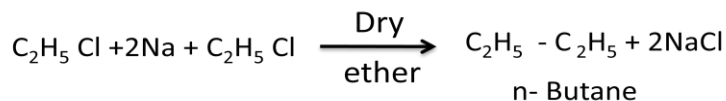


g. Action with sodium:

Two molecules of alkyl halide react with metallic sodium in of ether to form higher alkanes. This reaction is called Wurtz reaction.

Example:

Ethyl chloride gives n – butane on Wurtz reaction.

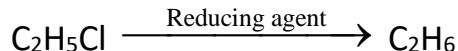


h. Reduction:

Haloalkanes are reduced to alkanes by many reagents like.

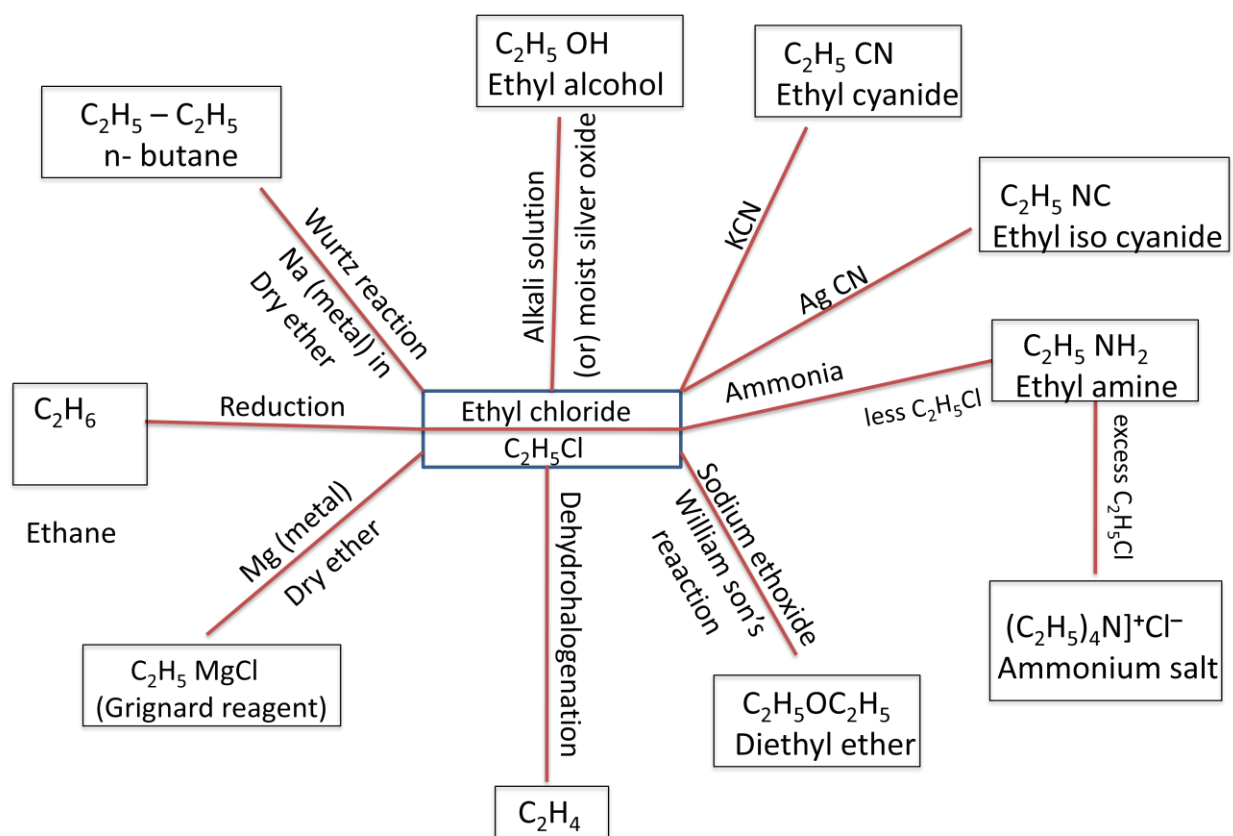
- i. $\text{Zn} + \text{HCl}$, $\text{Sn} + \text{HCl}$
- ii. Lithium aluminium hydride [LiAlH_4] or Sodium borohydride [NaBH_4]

iii. H_2 in the presence of nickel or palladium



Ethyl chloride is an important compound from which a variety of products can be prepared. These reactions are summarised in the chart given.

Summary of properties of ethyl chloride:



Ethyl chloride is used:

- as a refrigerant
- as a local anesthetic
- as a solvent
- as ethylating agent in the preparation of tetraethyl lead [TEL]
- in the preparation of Grignard's reagent

Assignment questions:

1. Write any five chemical properties of ethyl chloride giving proper equations.
2. What happens when thionylchloride reacts with ethyl alcohol? Write the equation.
3. What are the products formed when ethyl chloride is treated with
 - a. Na
 - b. NH_3

Give the equations.

4. Write any two uses of ethyl chloride.

SAQs:

1. The oxyacid formed, when ethyl alcohol is treated with PCl_3 is
 - a. H_3PO_4
 - b. HOCl
 - c. H_3PO_3
 - d. HPO_3

Solution: c)

2. In which of the following reactions $\text{C}_2\text{H}_5\text{Cl}$ is obtained?
 - a. $\text{C}_2\text{H}_4 + \text{HCl}$
 - b. $\text{C}_2\text{H}_2 + \text{HCl}$
 - c. $\text{C}_2\text{H}_6 + \text{HCl}$
 - d. $\text{CH}_4 + \text{Cl}_2$

Solution: a)

3. Pick up the correct statement about ethyl chloride. It
 - a. Forms H - bonding
 - b. is freely soluble in water
 - c. is soluble in organic solvents
 - d. Has no polar bond

Solution: c)

4. Ethyl chloride on treatment with a suspension of Ag_2O in moist ether gives
- Ethanol
 - Ethanal
 - Ethane
 - Ethoxy ethane

Solution: a)

5. The reaction between ethyl chloride and sodium, in dry ether, to form n – butane is called
- Friedel – Craft’s reaction
 - Wurtz reaction
 - Cannizzaro’s reaction
 - Williamson’s reaction

Solution: b)

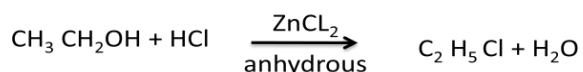
LAQs:

1. How is ethyl chloride formed in Groove’s process? Give equation.

Solution:

Groove’s process:

Primary alcohols produce chloroalkanes when hydrochloric acid vapours are passed through the alcohol in the presence of anhydrous zinc chloride.



Pyridine, dimethyl amine and conc. Sulphuric acid are also used as catalyst for the above reaction.

ZnCl_2 , is a Lewis acid it readily coordinates with the oxygen atom of the alcohols. As a result, the C– O bond weakens and breaks to form Carbocation. This reacts with chloride ion to form chloroalkanes. Thus, anhydrous ZnCl_2 helps in the cleavage of the C– O bond.

2. What are the products formed when ethyl chloride is treated with
- KCN
 - Ag CN. Give the equations.

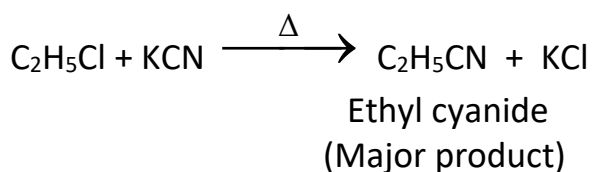
Solution:

Substitution by cyanide and isocyanide group takes place.

Haloalkanes react with an alcoholic solution of potassium cyanide to give alkylcyanides as the major products along with small amounts of alkyl isocyanides.

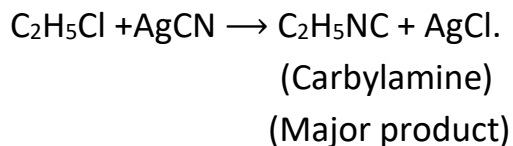
Example:

Ethyl chloride gives ethyl cyanide with KCN.



Isocyanides are obtained when haloalkanes are treated with alcoholic silver cyanide (AgCN). These are called carbylamines and have extremely unpleasant smell.

Example:



Problem set:

1. Alcoholic solution of KOH is used for
- Dehalogenation
 - Dehydrohalogenation
 - Dehydration

d. Dehydrogenation

Solution: b)

2. Which of the following metals is used in the preparation of Grignard reagent?

- a. Zn
- b. Ca
- c. Mg
- d. Fe

Solution: c)

3. Which of the following reagents will produce isocyanide when treated with ethyl chloride?

- a. KCN
- b. NaCN
- c. AgCN
- d. AgNO₂

Solution: c)

4. Ethyl chloride can be reduced to ethane by

- a. LiAlH₄
- b. Zn + HCl
- c. H₂/Ni
- d. All the above

Solution: d)

5. Write any two physical properties of ethyl chloride.

Solution:

Physical properties:

It is a colourless gas with a pleasant odour. Its boiling point is 286K, and its density is 0.91 g/ml. It is soluble in organic solvents like carbon tetrachloride,

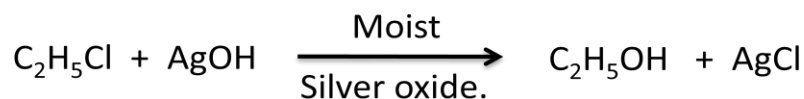
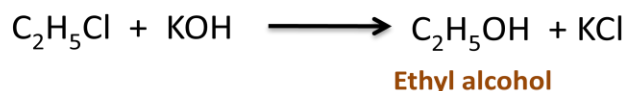
but almost insoluble in water. As C–Cl bond is covalent it does not give Cl[–] ions in solution. Hence it does not form a precipitate with silver nitrate solution.

6. What happens when ethyl chloride is treated with
- Aqueous KOH (KOH_{aq})
 - C₂H₅ONa
 - Mg
 - Zn/HCl

Solution:

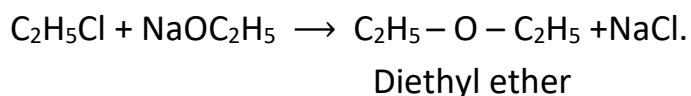
a. Replacement by hydroxyl group [Formation of alcohols]

On treatment with aqueous solution of KOH or moist silver oxide [Ag₂O/H₂O] chloro ethane gives alcohol. For example



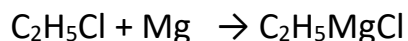
b. Replacement by alkoxy group:

Ethyl chloride reacts with sodium ethoxide to form a diethylether. This is called Williamson's synthesis of ether. Similarly any other alkyl halide, on treatment with sodium alkoxide, undergoes with Wurtz-Fittig's reaction.



c. Action with magnesium [formation of Grignard reagent]:

When a solution of an alkyl halide, in dry ether, is treated with magnesium metal, an alkyl magnesium halide is formed.

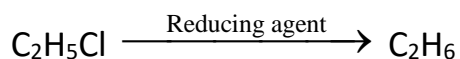


diether
[Ethyl magnesium chloride]
Grignard reagent

d. Reduction:

Haloalkanes are reduced to alkanes by many reagents like.

- a. $\text{Zn} + \text{HCl}$, $\text{Sn} + \text{HCl}$
- b. Lithium aluminium hydride [LiAlH_4] or Sodium borohydride [NaBH_4]
- c. H_2 in the presence of nickel or palladium



Exercise questions:

1. What happens when n – propyl bromide is treated with alcoholic KOH?
2. How will you distinguish between an alkyl halide and an alkene?
3. How will you distinguish between ethyl chloride and vinyl chloride?
4. How will you synthesise isopropyl bromide from n – propyl bromide?
5. How will you synthesise n – propyl bromide from iso – propyl bromide?
6. How will you synthesise ethyl bromide into propionic acid?

Solutions:

1. Propene is formed.



- 2.

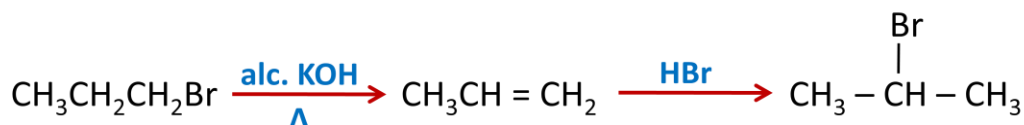
a. Alkyl halides give a positive Beilstein test:

In this test a small loop of copper wire is heated in a flame until any impurities are consumed and the flame has become colourless. A drop or a small amount of the unknown compound is then placed on the loop and the loop is again heated in the flame. A green flame shows the presence of halogen. Alkenes do not give this test.

- b. Alkyl halides give a precipitate of AgX when warmed with alc. AgNO_3 solution. Alkenes do not react with AgNO_3 .

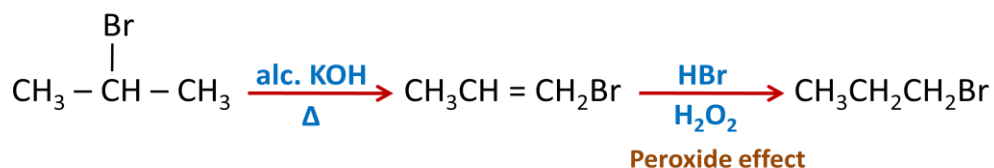
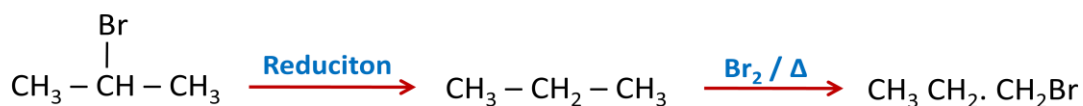


3. Ethyl chloride, $\text{C}_2\text{H}_5\text{Cl}$, reacts with alc. AgNO_3 to give a ppt of AgCl . Vinyl chloride does not give this test.
- 4.

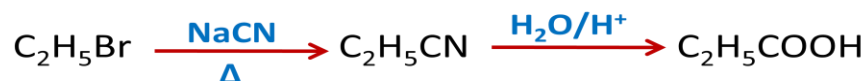


According to Markovnikov's rule

5.



6.



Haloalkanes and Haloarenes

Module 32.3: Chloroform-preparation, properties & uses

Chloroform is an organic compound with molecular formula CHCl_3 . It is a member of a group of compounds known as trihalomethanes.

Preparation:

Laboratory method for chloroform preparation:

Ethanol (ethyl alcohol) or propanone (acetone) when treated with bleaching powder gives chloroform. This reaction is known as haloform reaction. The reactions are represented as shown below.

a. From ethanol:

The bleaching powder reacts with water giving chlorine and calcium hydroxide.



The reaction with alcohol proceeds in following steps:

First step is the oxidation of ethyl alcohol to give acetaldehyde.



Second step is chlorination of acetaldehyde to form chloral (trichloroacetaldehyde.)



Lastly, the reaction of chloral with lime gives chloroform.



b. From propanone (or acetone):

The bleaching powder reacts with water giving chlorine and calcium hydroxide.



Then the chlorination of acetone to give trichloroacetone takes place

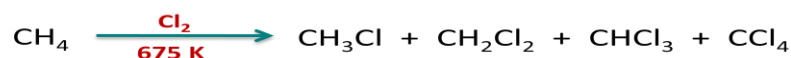


Lastly, reaction of trichloroacetone with lime takes place to form chloroform.



c. By chlorination of methane:

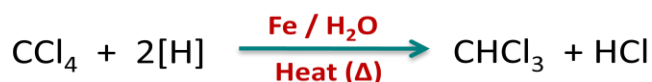
On an industrial scale, chloroform can be prepared by chlorination of methane at 675 K. A mixture of chloro compounds is obtained.



Chloroform is separated from this mixture of products by fractional distillation.

d. By reduction of carbon tetrachloride:

On an industrial scale chloroform can also be prepared by reducing carbon tetrachloride with iron filings and steam.



e. Pure chloroform:

It is prepared by distilling chloral hydrate with concentrated solution of caustic soda.



Physical properties of chloroform:

- Chloroform is a colorless, 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 solvents such as ethanol and ether.
- The boiling point is 334 K and freezing point is 210 K.
- It is a good solvent for oils, fats and waxes.
- It is a poisonous compound, the vapors of which, when inhaled, cause unconsciousness. Hence, chloroform is used as an anesthetic.

Chemical properties of chloroform:

The important chemical properties of chloroform are given below:

a. Oxidation:

In the presence of air and light chloroform is slowly oxidized into a poisonous compound, phosgene (or carbonyl chloride).

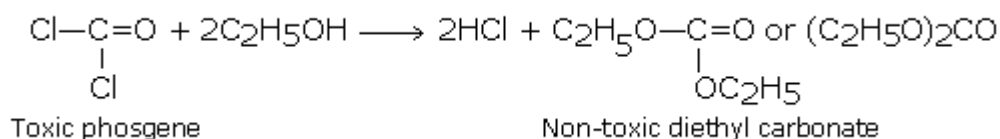


Since phosgene is very poisonous, its presence makes chloroform unfit for use as an anesthetic.

b. Preservation of chloroform:

If chloroform is to be used for anesthetic purposes, its slow oxidation to phosgene must be prevented. The following precautions are taken to keep chloroform pure:

- It should be stored in dark colored bottles to protect it from sunlight.
- The bottles containing chloroform are completely filled up to the brim and are properly stoppered to keep out air.
- A small amount of 0.6 to 1% alcohol is added to the bottles of chloroform. This reacts with phosgene that may be formed during storage to form non-toxic, harmless diethyl carbonate.



c. Reduction:

Chloroform gets reduced with zinc and hydrochloric acid to form methylene-chloride. If the reduction is carried with zinc dust and water, methane is obtained.



d. Nitration:

Chloroform reacts with concentrated nitric acid to form nitro-chloroform or chloropicrin.



Chloropicrin is used as an insecticide and war gas.

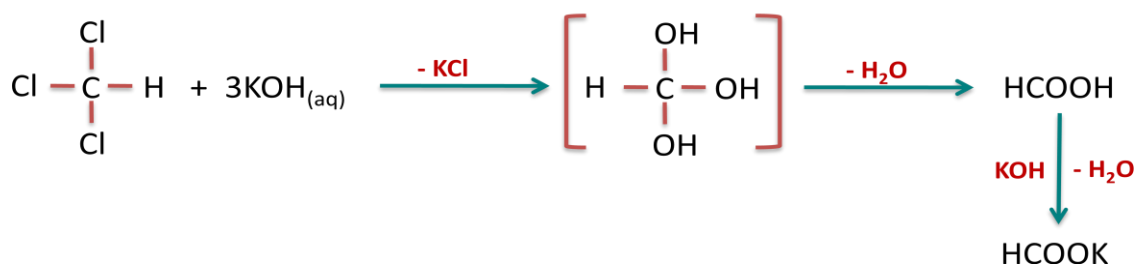
e. Chlorination:

Chlorination of chloroform with chlorine in the presence of diffused sunlight gives carbon tetrachloride



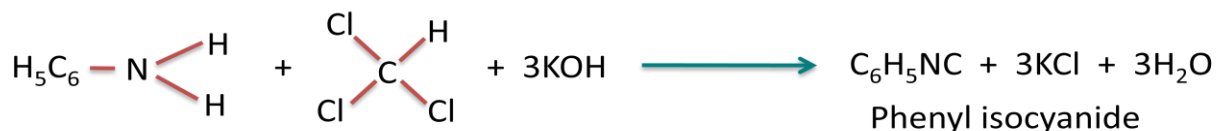
f. Hydrolysis:

Chloroform gives potassium-formate, on warming with concentrated aqueous or alcoholic potassium hydroxide.



g. Carbylamine reaction:

Chloroform reacts with primary amines (both aliphatic and aromatic) and alcoholic caustic potash, to give an isocyanide, which is commonly known as carbylamine. It has an extremely unpleasant smell and the reaction is used as a test for primary amines.



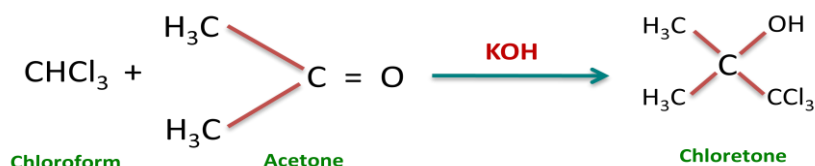
h. Reaction with silver powder:

Chloroform is converted into acetylene on warming with silver powder.



i. Condensation with acetone:

Chloroform combines with acetone in the presence of potassium hydroxide to give chloretone, which is used as a sleep inducing (hypnotic) drug.



j. Reaction with phenol:

Chloroform reacts with phenol in sodium hydroxide at 340K to give salicylaldehyde.



This reaction is called '*Reimer -Tiemann reaction.*'

Uses:

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 anesthetic in surgery but has been replaced by less toxic, safer anesthetics, such as ether. As might be expected from its use as an anesthetic, 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 metabolized to phosgene) and to the kidneys, and some people develop sores when the skin is immersed in chloroform. Chloroform is slowly oxidized 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.

Some useful halogen derivatives

1. Dichloromethane:

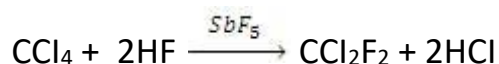
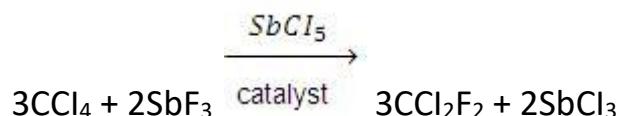
Dichloromethane is widely used as a solvent as a paint remover, as a propellant in aerosols, and as a process solvent in the manufacture of drugs. It is also used as a metal cleaning and finishing solvent. Methylene chloride harms the human central nervous system. Exposure to lower levels of methylene 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.

2. 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.

3. Freons :

The chloro fluoro derivatives of methane and ethane are called freons. Some of the derivatives are: CHF_2Cl (monochlorodifluoromethane), CF_2Cl_2 (dichloro difluoro methane), $\text{HCF}_2\text{CHCl}_2$ (1, 1-dichloro 2, 2-difluoroethane). These are non-inflammable, colourless, non-toxic and low boiling liquids. These are stable upto 550°C . The most important and useful derivative is CF_2Cl_2 which is commonly known as **Freon** or **Freon-12**. Freon or freon-12 (CF_2Cl_2) is prepared by treating carbon tetrachloride with antimony trifluoride in the presence of antimony penta chloride (a catalyst), or by reacting carbon tetrachloride with hydrofluoric acid in presence of antimony penta fluoride.

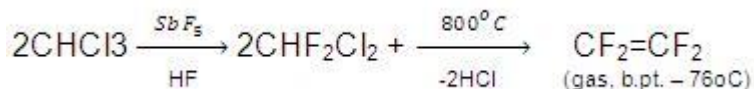


Under normal conditions Freon is a gas. (b.pt. -29.8°C). It can easily be liquefied. It is chemically inert and is used in air-conditioning and in domestic refrigerators.

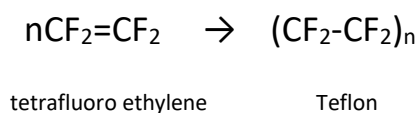
Note : Freon-14 is CF_4 , Freon-13 is CF_3Cl , Freon-11 is CFCl_3 . All these are used as refrigerant.

4. Teflon:

A plastic like substance produced by the polymerization of tetrafluoro-ethylene ($\text{CF}_2=\text{CF}_2$). Tetrafluoro-ethylene is formed when chloroform is treated with antimony trifluoride and hydrofluoric acid.



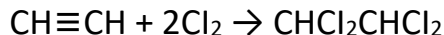
On polymerization, tetrafluoro ethylene forms a plastic-like material which is called teflon.



Teflon is chemically inert substances. It is not affected by strong acids and even by boiling aquaregia. It is stable at high temperature and thus, used for electrical insulation and preparation of gasket materials.

3. Acetylene tetrachloride (Westron), $\text{CHCl}_2\text{CHCl}_2$:

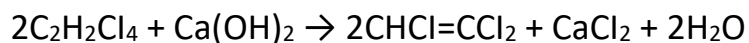
Acetylene tetrachloride is also known as sym (tetrachloroethane). It is prepared by the action of chlorine on acetylene in presence of a catalyst such as ferric chloride, aluminium chloride, iron, quartz or kieselguhr.



In absence of catalyst, the reaction between chlorine and acetylene is highly explosive producing carbon and HCl. The reaction is less violent in presence of catalyst.

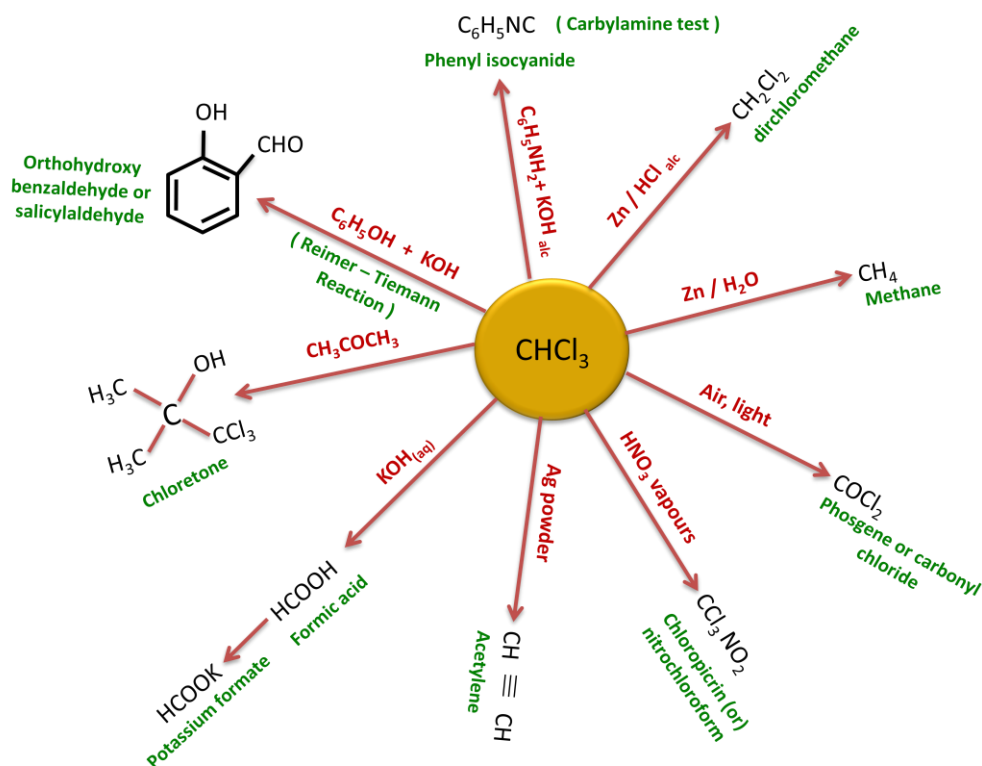
It is a heavy, non-inflammable toxic liquid with smell like CHCl_3 . It is insoluble in water but soluble in organic solvents.

On further chlorination, it forms penta and hexachloroethane. On heating with lime (calcium hydroxide), it is converted to a useful product **westrosol** ($\text{CCl}_2=\text{CHCl}$)



Both westron and westrosol are used as solvent for oils, fats and varnishes.

Summary of the reactions of reactions:



Assignment questions:

1. How is chloroform converted to acetylene? Give equation.
2. How is potassium formate obtained from chloroform? Give equation.
3. Write two physical properties of chloroform
4. Write any two uses of chloroform

SAQs:

1. Pure chloroform is prepared by distilling concentrated NaOH solution with
 - a. $\text{C}_2\text{H}_5\text{OH}$
 - b. CH_3CHO
 - c. CH_3COCH_3
 - d. $\text{CCl}_3\text{CH}(\text{OH})_2$

Solution: d)

2. Which of the following statements is wrong about chloroform? it
- is insoluble in water but soluble in organic solvents
 - is lighter than water
 - burns with green flame
 - is a sweet smelling, colorless liquid

Solution: b)

3. Chloroform on reduction with Zn and HCl in alcohol gives
- Formic acid
 - Methane
 - Methylene chloride
 - Methylchloride

Solution: c)

4. Chloroform is treated with phenol in basic medium. The product formed is
- Chlorobenzene
 - Chlorophenol
 - Benzoic acid
 - Salicylaldehyde

Solution: d)

LAQs:

1. What happens when chloral hydrate is Distiled with caustic soda? Give equation

Solution:

Pure chloroform is formed.

It is prepared by distilling chloral hydrate with a concentrated solution of caustic soda.



2. How is chloroform obtained from
- Ethyl alcohol
 - Acetone. Give equations

Solution:

From ethanol:

The bleaching powder reacts with water giving chlorine and calcium hydroxide :



The reaction proceeds in steps:

First step is the oxidation of ethyl alcohol to give acetaldehyde.



Second step is chlorination of acetaldehyde to form chloral (or trichloro acetaldehyde.)



Lastly, the reaction of chloral with lime gives chloroform.



From propanone (or acetone):

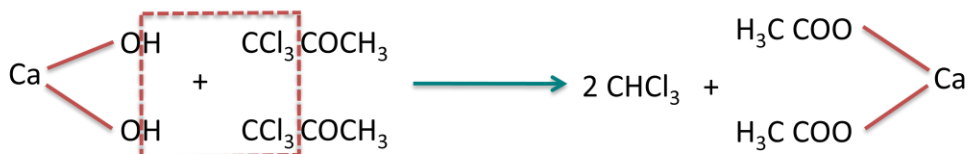
The bleaching powder reacts with water giving chlorine and calcium hydroxide :



Then the chlorination of acetone to give trichloroacetone takes place



Lastly, reaction of trichloroacetone with lime takes place to form chloroform.



Problem set:

1. Iso cyanide test is useful to detect

- a. Primary alcohol
- b. Primary amines
- c. Secondary alcohol
- d. Secondary amines

Solution: b)

2. In the preparation of chloroform from ethyl alcohol and bleaching powder, the compound that is not formed.
- a. Calcium acetate
 - b. Chloral
 - c. Calcium formate
 - d. Acetaldehyde

Solution: a)

3. Chloroform is used as a
- a. general anesthetic
 - b. solvent for fats and oils
 - c. preservative for biological specimens
 - d. All are correct

Solution: d)

4. What happens when chloroform reacts with
- i. Phenol in presence of an alkali
 - ii. Acetone in the presence of KOH
 - iii. HNO_3 vapours
 - iv. Metallic silver

Solution:

i. Reaction with phenol

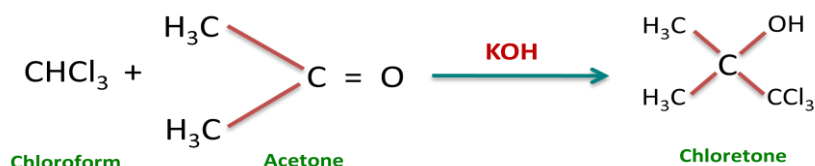
Chloroform reacts with phenol in sodium hydroxide at 340K to give salicylaldehyde.



This reaction is called '**Reimer -Tiemann reaction.**'

ii. Condensation with acetone

Chloroform combines with acetone in the presence of potassium hydroxide to give chloretone, which is used as a sleep inducing (hypnotic) drug.



iii. Nitration

Chloroform reacts with concentrated nitric acid to form nitro chloroform or chloropicrin.



Chloropicrin is used as an insecticide and war gas.

iv. Reaction with silver powder

Chloroform is converted into acetylene on warming with silver powder.



5. What is chloropicrin? How it is formed from chloroform? Give equations for the reactions

Solution:

Nitration

Chloroform reacts with concentrated nitric acid to form nitro chloroform or chloropicrin.



Chloropicrin is used as an insecticide and war gas.

Exercise questions:

1. What happens when ethyl alcohol is treated with bleaching powder?
2. What happens when chloroform is heated with ethylamine in the presence of alcoholic KOH?
3. How will you distinguish between chloroform and carbon tetrachloride?

4. What is phosgene? How it is formed from chloroform? Give equation for the reaction?
5. Why do we add 1% alcohol during preservation of chloroform?

Solutions:

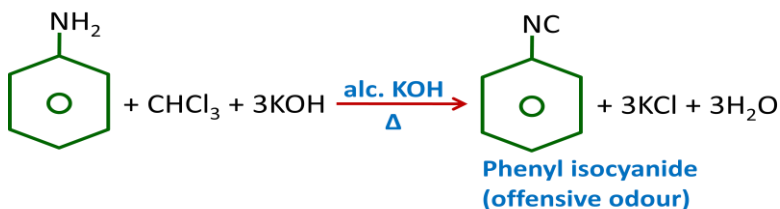
1. The reactions that take place are



2. Ethyl isocyanide is formed



3. When chloroform is heated with aniline and alcoholic KOH, offensive smell of isocyanide (or carbylamines) is observed. Carbon tetrachloride does not give this test.



Haloalkanes and Haloarenes

Module 32.4: Haloarenes-preparation, properties & uses

In organic chemistry, a halogenoarene, haloarene, or aryl halide, is an organic compound in which a halogen atom is bonded to a carbon atom which is a part of an aromatic ring. The haloarenes are studied separately from haloalkanes because they exhibit a lot of differences in methods of preparation and properties.

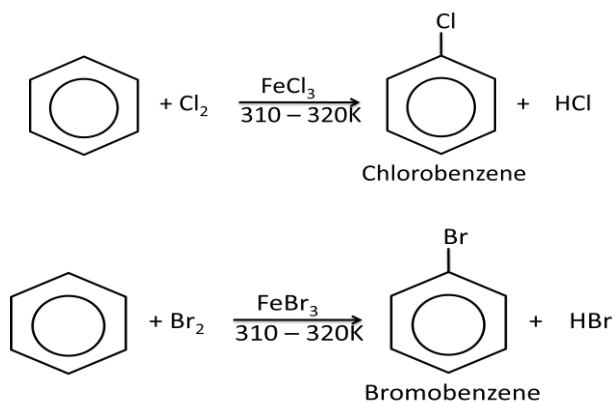
Preparation of haloarenes:

Haloarenes are prepared by many methods. The following are two of the methods.

i. Direct halogenation of aromatic ring

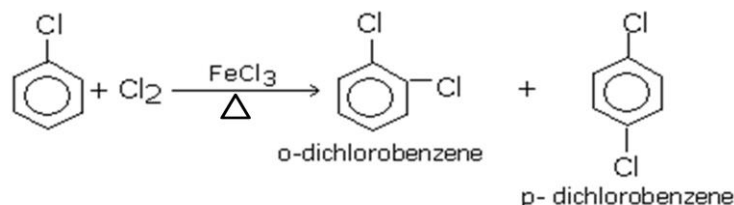
Direct chlorination or bromination of benzene or other aromatic hydrocarbon gives chloro benzene or bromobenzene or chloroarenes and bromoarenes. These reactions are carried out in the presence of Lewis acids such as anhydrous ferric or aluminium halides (FeCl_3 , FeBr_3 , AlCl_3) in the dark, at ordinary temperatures (310 – 320 K).

The Lewis acid acts as a catalyst or a halogen carrier. Its function is to carry the halogen to the aromatic hydrocarbon. In actual practice, iron filings in the presence of chlorine or bromine are commonly used. The halogens react with iron filings to form corresponding Lewis acid.

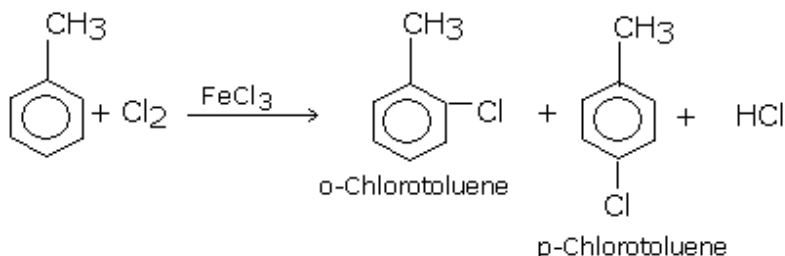


Halogenation of arenes is an electrophilic substitution reaction. The function of the halogen carrier is to generate 'electrophile' which attacks the benzene ring to form the product.

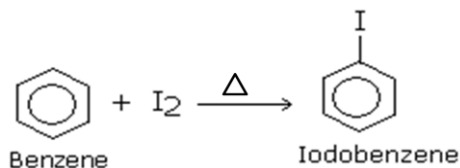
With excess halogen, the second halogen also gets introduced in to the ring at ortho and para positions with respect to the first halogen because halogens are ortho and para directing groups.



Similarly, chlorination of toluene gives a mixture of ortho and parachlorotoluene because -CH₃ group in toluene is ortho and para directing.



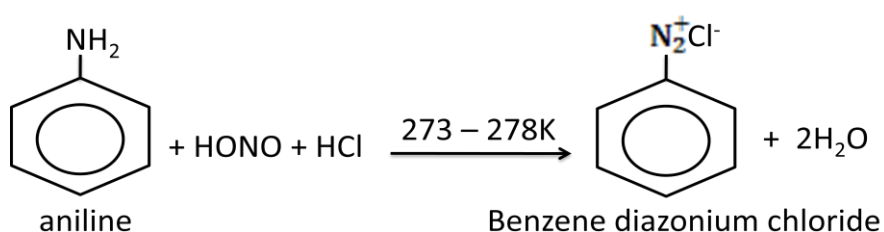
The reaction with fluorine is violent and cannot be controlled. Therefore, fluoroarenes cannot be prepared by direct fluorination of aromatic hydrocarbon. Bromo compounds can be prepared in a way similar to chlorination, by reacting with Br₂ in the presence of FeBr₃. Iodoarenes are also difficult to prepare by direct iodination because the reaction is reversible and HI produced is a strong reducing agent to reduce iodobenzene back to benzene.



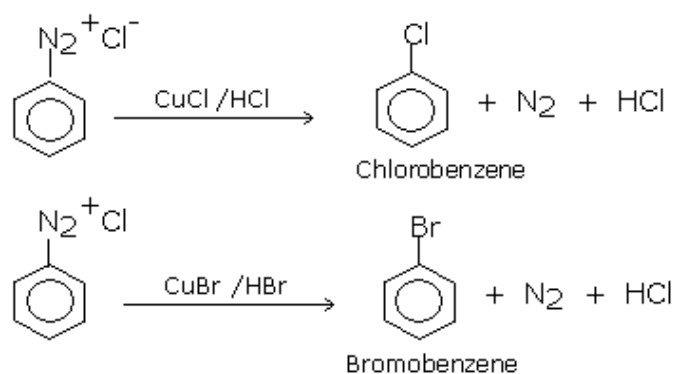
This reaction is carried out in the presence of an oxidizing agent like iodic acid or nitric acid, they oxidize HI formed in the reaction to iodine and favour the forward reaction.

ii. Sandmeyer's reaction

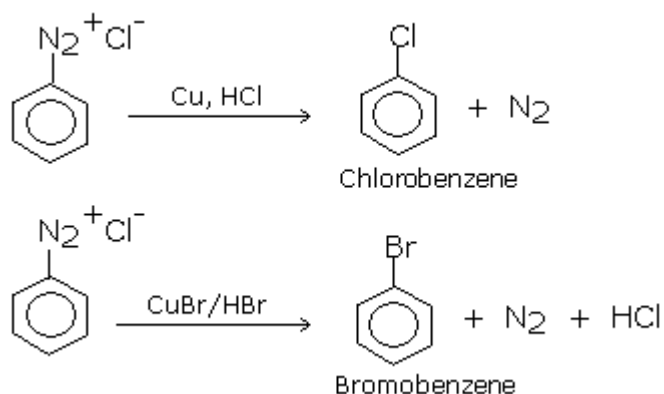
This reaction consists of treating freshly prepared diazonium salt solution with cuprous chloride or cuprous bromide. The copper salt is dissolved in the corresponding halogen acids. Chloro and bromoarenes are formed. Diazonium salts required for this purpose are prepared by treating ice-cold solution of amino derivatives of arenes with excess of dilute HCl and with an aqueous solution of sodium nitrite at low temperature (0-5°C). This reaction is known as diazotization reaction.



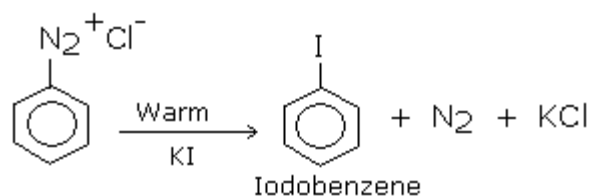
The benzene diazonium salt is used for preparing aryl halides as:



The Sandmeyer reaction has been modified in 'Gattermann reaction'. In this reaction Copper powder is used in the presence of corresponding halogen acid (HCl or HBr) in place of cuprous halide (CuCl, CuBr).



Warming the diazonium salt solution with aqueous KI solution gives iodoarenes. This is the best method for introducing iodine into benzene ring.



Physical properties of haloarenes or aryl halides

- Haloarenes are colorless liquids or crystalline solids.
- Aryl halides are heavier than water. And they are insoluble in water but soluble in organic solvents.
- The melting and boiling points of aryl halides are nearly the same as those of alkyl halides containing the same number of carbon atoms. Boiling points of monohalogen derivatives of benzene are in the order:
iodo>bromo>chloro>fluoro

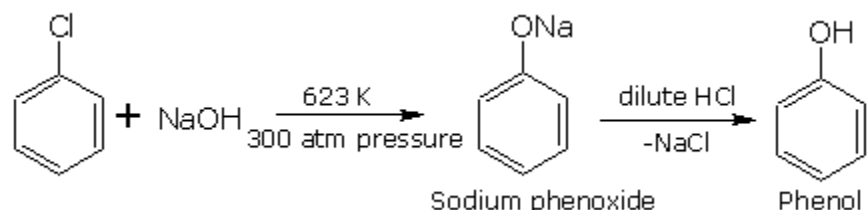
Name	Compound	Boiling point
Chlorobenzene	C ₆ H ₅ Cl	132°C
Bromobenzene	C ₆ H ₅ Br	156°C
Iodobenzene	C ₆ H ₅ I	189°C

Chemical properties of haloarenes

Haloarenes are chemically less reactive compared to haloalkanes. They can undergo the following reactions:

a. Replacement by hydroxy group (formation of phenol):

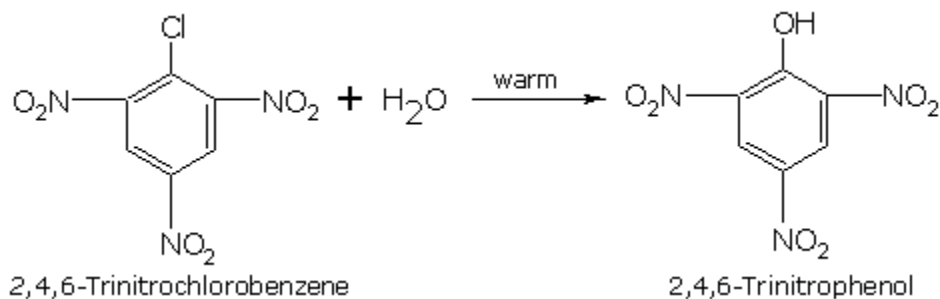
When aryl halides are heated, at 623K and under pressure (300 atm), with aqueous solution of sodium hydroxide, the halogen atom is replaced by hydroxyl group forming phenol. Firstly sodium phenoxide is formed, which on acidification gives phenol.



This reaction is used in the manufacture of phenol by Dow's process.

b. Effect of substituent's on the reactivity of haloarenes:

The reactivity of haloarenes is markedly affected by the presence of certain groups at certain positions in the ring. The presence of electron withdrawing groups such as $-\text{NO}_2$, $-\text{CN}$, $-\text{COOH}$, etc. at 'o' and 'p' positions to the halogen atom, greatly activates the halogen towards further nucleophilic substitution reactions. For example, Chlorobenzene is converted into phenol by aqueous NaOH only at temperatures above 573 K, whereas p-chloronitrobenzene is converted into nitro phenol by aqueous NaOH at a lower temperature of 433K. As the number of ortho and para nitro groups on the ring is increased the reactivity increases. The following reactions will clear these points.



Nitro group meta to the chlorine has no significant effect on the reactivity.

c. Ring substitution or electrophilic substitution reactions:

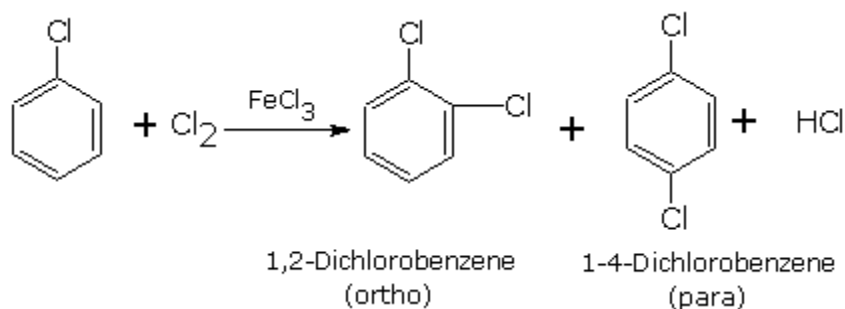
The halogen atom is ortho and para directing and therefore, substitution takes place at ortho and para positions giving electrophilic substitution reactions in the benzene ring.

In the resonance structures of Chlorobenzene the ortho and para positions get negatively charge, i.e. the electron density is relatively more at ortho and para positions. The incoming electrophile is more likely to attack at these positions. But, because of steric hindrance at the ortho position, the para-product usually predominates over the ortho product. Also, the halogen atom has -I effect because it is an electron withdrawing group. As a result, it tends to deactivate the benzene ring. Therefore, the electrophilic substitution reactions of Chlorobenzene occur slowly and take place only under drastic conditions compared to benzene. Thus,

- Haloarenes undergo electrophilic substitution reactions slowly as compared to benzene.
- Halogen group is ortho and para directing (para-product usually predominates over the ortho product).

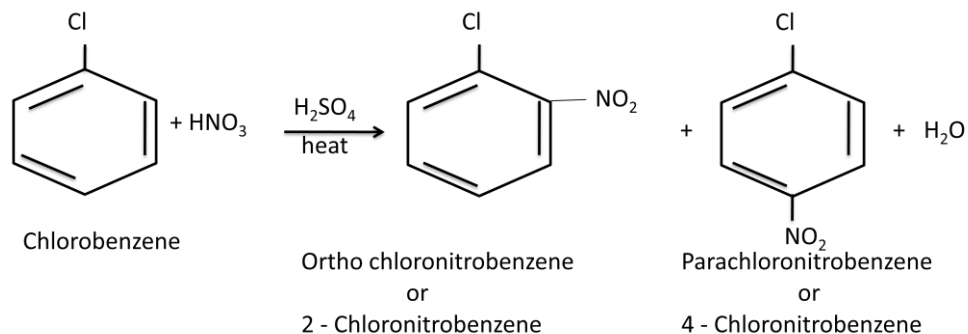
i. Halogenation

Haloarenes react with halogens, in the presence of ferric salt as catalyst, to give ortho and para isomers.



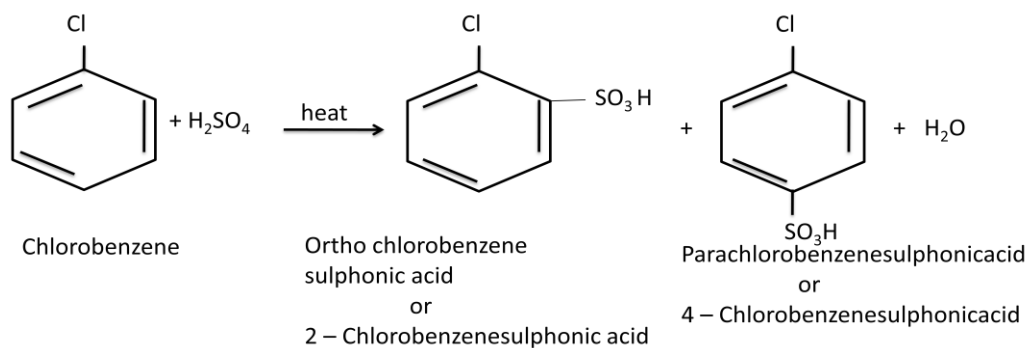
ii. Nitration

Haloarenes react with nitration mixture (concentrated HNO_3 in the presence of concentrated H_2SO_4) give o- and p-substituted derivatives.



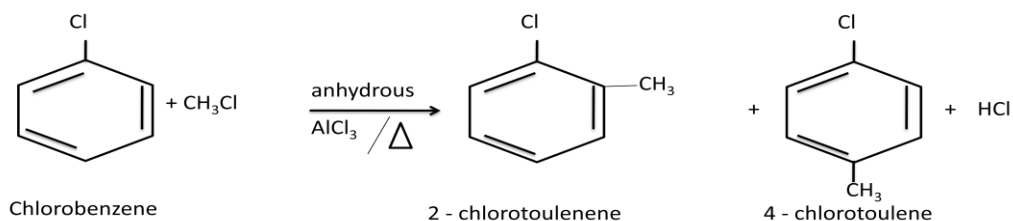
iii. Sulphonation

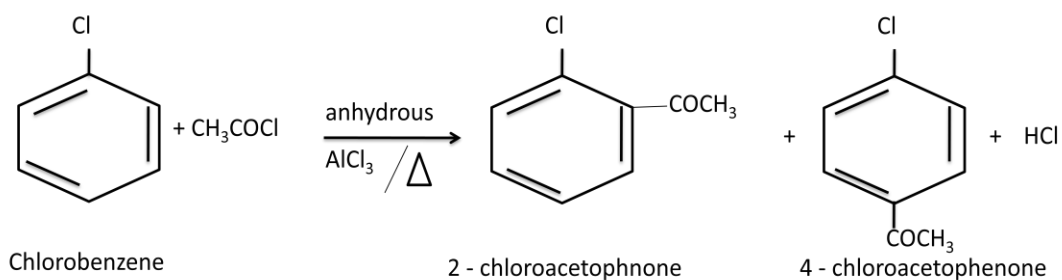
Sulphonation occurs when a haloarene is treated with concentrated H_2SO_4 .



iv. Alkylation and acylation

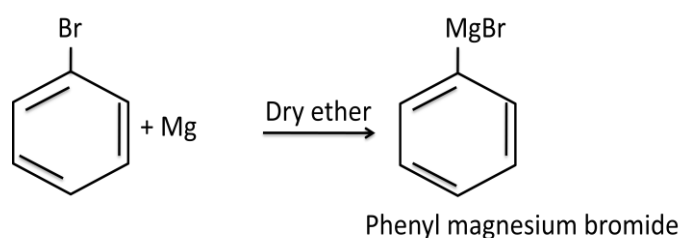
The alkylation and acylation reaction, known as 'Friedel-Craft's reaction, is carried out by treating haloarene with alkyl chloride or acyl chloride in the presence of a catalyst like anhydrous aluminium chloride. For example,



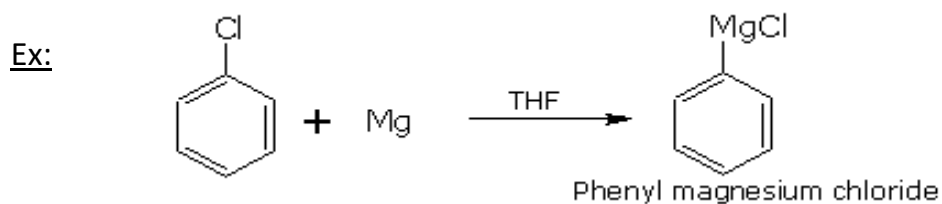


v. Reaction of magnesium

Aryl bromides and iodides react with magnesium in dry ether to form Grignard reagent.

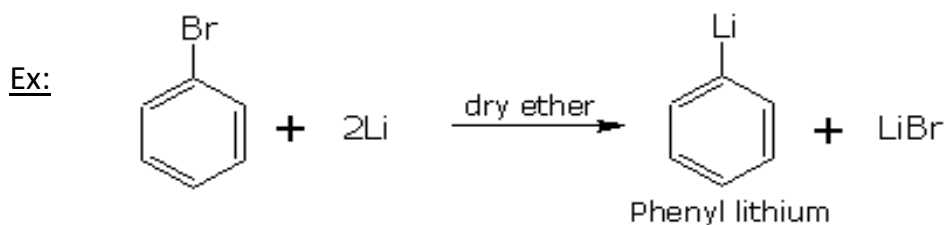


Chlorobenzene reacts with magnesium in tetrahydrofuran (THF) solvent.



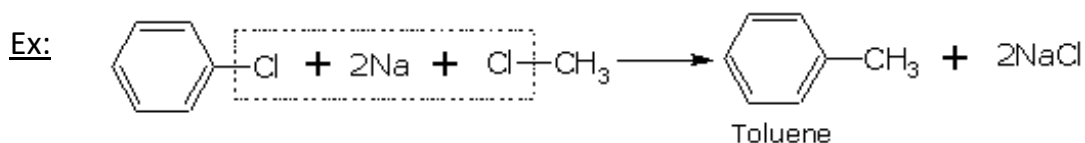
vi. Reaction with lithium

Bromo and iodoarenes react with lithium metal in dry ether to form corresponding organo metallic compounds.

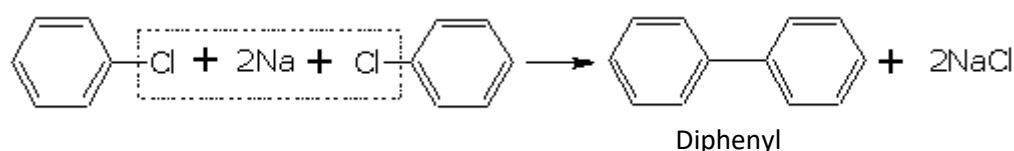


vii. Reaction with sodium

Aryl halides undergo 'Wurtz- Fittig reaction' when heated with alkyl halide in the presence of sodium in dry ether. Halogen atom is replaced by an alkyl group and an arene is formed.

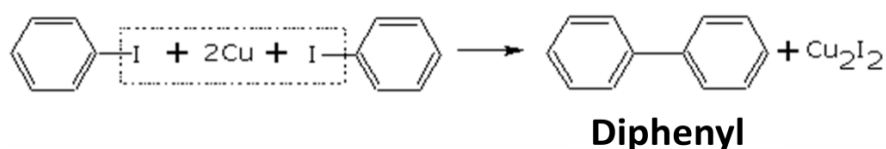


However, when halobenzenes react with sodium in dry ether, diphenyl is formed. This reaction is called 'Fittig reaction'.



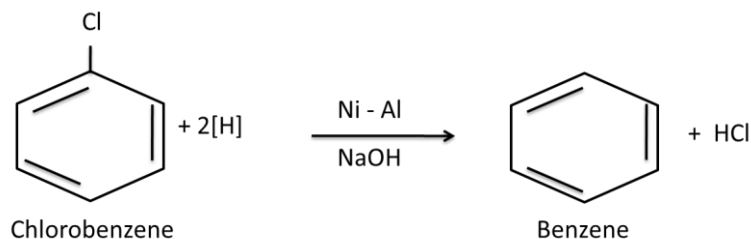
viii. Reaction with copper powder

Iodobenzene gives diphenyl when heated with copper powder in a sealed tube. This reaction is called 'Ullmann reaction'.



ix. Reduction

With LiAlH_4 or nickel aluminium alloy (Ni-Al), haloarenes undergo reduction to hydrocarbons in the presence of an alkali. The reduction is brought about by nascent hydrogen.



Assignment questions

1. How is chlorobenzene prepared in the laboratory?
2. Give the equations for the action of the following on chlorobenzene. Write the suitable conditions.
 - i. H_2SO_4
 - ii. CH_3Cl
 - iii. Mg
 - iv. Na
3. Explain why?
 - a. Chlorine is ortho-para directing although it has -I effect.
 - b. 2, 4-dinitrochlorobenzene undergoes nucleophilic substitution reactions faster than chlorobenzene.
4. Write the reactions with necessary equations for the following conversions:
 - a. Benzene to chlorobenzene.
 - b. Chlorobenzene \rightarrow phenol.
 - c. Chlorobenzene \rightarrow picric acid.

Example set:

1. Benzene undergoes chlorination, in the presence of ferric chloride, at
 - a. Low temperature
 - b. High temperature
 - c. Ordinary temperature
 - d. All temperature

Solution:c)

2. The reaction
$$\text{C}_6\text{H}_5\text{N}_2\text{Cl} \xrightarrow{\text{Cu/HCl}} \text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{N}_2$$
 is called
 - a. Wurtz reaction
 - b. Sandmeyer's reaction
 - c. Perkin's reaction
 - d. Cannizaro reaction

Solution: b)

3. Pick up the correct statement about aryl halides. They
- Form H-bonding
 - are soluble in water
 - are soluble in organic solvents
 - do not contain any polar bond

Solution: c)

4. Chlorobenzene, on heating with NaOH at 300°C under pressure, gives
- Phenol
 - Benzaldehyde
 - Benzoyl dehyde
 - Salicylaldehyde

Solution: a)

LAQs:

1. Explain the preparation of chlorobenzene from
- Benzene
 - Aniline

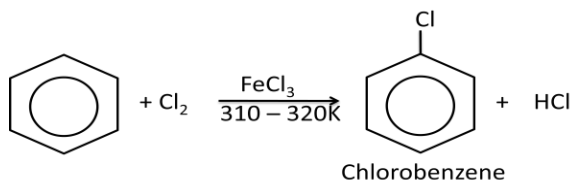
Solution:

a. Direct halogenation of aromatic ring:

Direct chlorination or bromination of benzene or other aromatic hydrocarbon gives chloro benzene or bromobenzene or chloroarenes and bromoarenes.

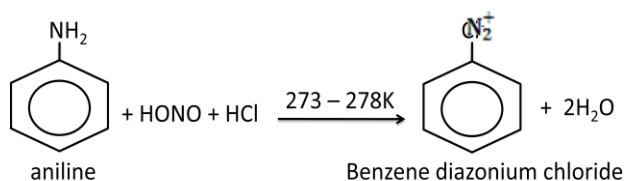
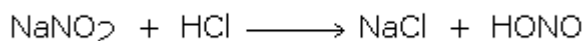
These reactions are carried out in the presence of Lewis acids such as anhydrous ferric or aluminium halides (FeCl_3 , FeBr_3 , AlCl_3) in the dark, at ordinary temperatures (310 – 320 K).

The Lewis acid acts as a catalyst or a halogen carrier. Its function is to carry the halogen to the aromatic hydrocarbon. In actual practice, iron filings in the presence of chlorine or bromine are commonly used. The halogens react with iron filings to form corresponding Lewis acid.

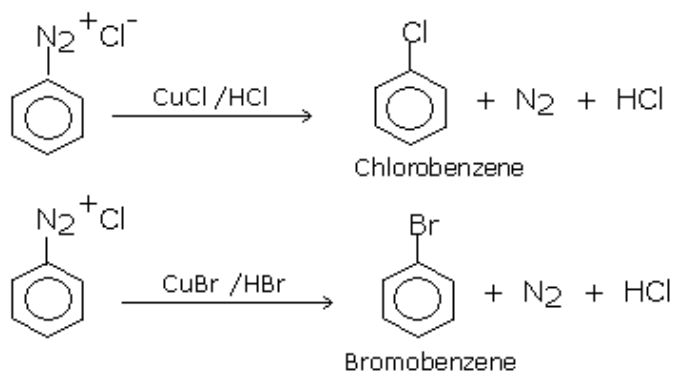


b. Sandmeyer's reaction:

This reaction consists of treating freshly prepared diazonium salt solution with cuprous chloride or cuprous bromide. The copper salt is dissolved in the corresponding halogen acids. Chloro and bromoarenes are formed. Diazonium salts required for this purpose are prepared by treating ice-cold solution of amino derivatives of arenes with excess of dilute HCl and with an aqueous solution of sodium nitrite at low temperature (0-5°C). This reaction is known as diazotization reaction.



The benzene diazonium salt is used for preparing aryl halides as:



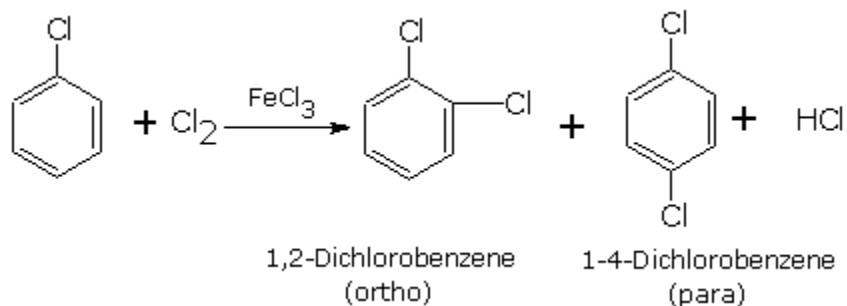
The Sandmeyer reaction has been modified in 'Gattermann reaction'. In this reaction Copper powder is used in the presence of corresponding halogen acid (HCl or HBr) in place of cuprous halide (CuCl, CuBr).

2. Write any 3 properties of chlorobenzene. What is the directive influence of a halogen on electrophilic substitution reaction of chlorobenzene?

Solution:

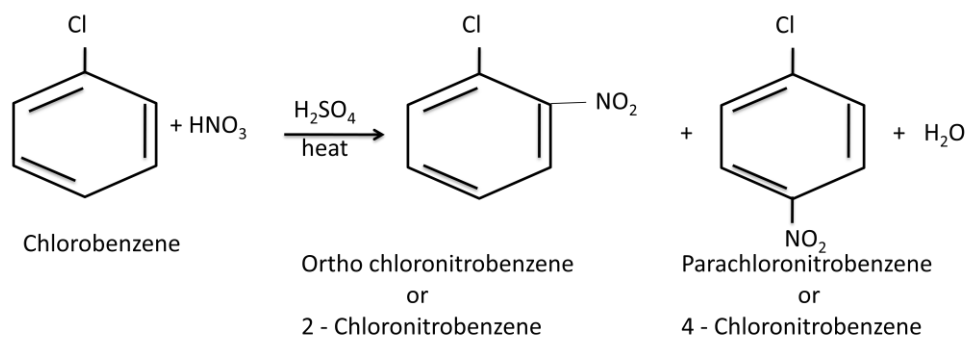
i. Halogenation

Haloarenes react with halogens, in the presence of ferric salt as catalyst, to give ortho and para isomers.



ii. Nitration

Haloarenes react with nitration mixture (concentrated HNO_3 in the presence of concentrated H_2SO_4) and give o-, and p - substituted derivatives.



iii. Sulphonation

Sulphonation occurs when a haloarene is treated with concentrated H_2SO_4 .

Solution:d)

4. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides. This is due to
- the formation of less stable carbonium ion
 - resonance stabilization
 - longer carbon – halogen bond
 - the inductive effect

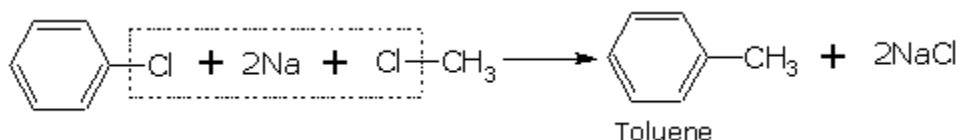
Solution:b)

5. What is the product obtained when chlorobenzene is heated with CH_3Cl in the presence of sodium and dry ether?

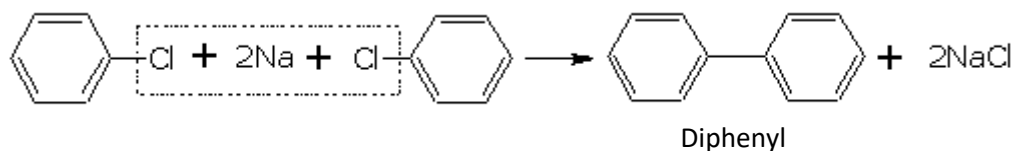
Solution:

Reaction with sodium

Aryl halides undergo 'Wurtz - Fittig reaction' when heated with alkyl halide in the presence of sodium in anhydrous ether. Halogen atom is replaced by an alkyl group and an arene is formed.



However, when halobenzenes react with sodium in dry ether, diphenyl is formed. This reaction is called 'Fittig reaction'.

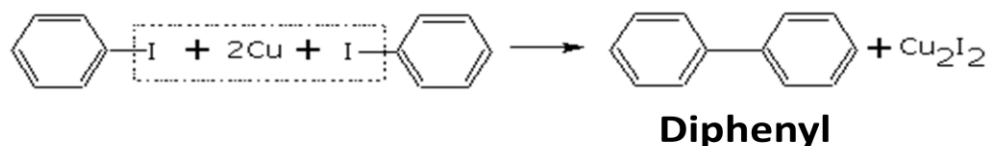


6. Explain Ullmann reaction.

Solution:

Reaction with copper powder:

Iodobenzene gives diphenyl when heated with copper powder in a sealed tube. This reaction is called 'Ullmann reaction'.



Exercise problems:

1. How will you distinguish between chlorobenzene and benzyl chloride?

Solution:

The following visual tests can be used:

- a. Benzyl chloride reacts with alcoholic AgNO_3 solution to form a precipitate of AgCl . Chlorobenzene does not react



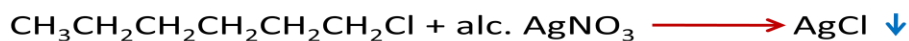
- b. Benzyl chloride is oxidized with alkaline KMnO_4 to form benzoic acid. Purple colour of KMnO_4 disappears. Chlorobenzene does not react.



2. How will you distinguish between chloroform and n – hexyl chloride?

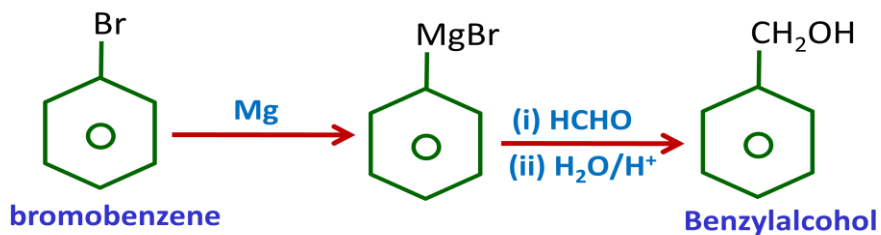
Solution:

n – Hexyl chloride reacts with alc. AgNO_3 solution to give a precipitate of AgCl . Chlorobenzene does not react.



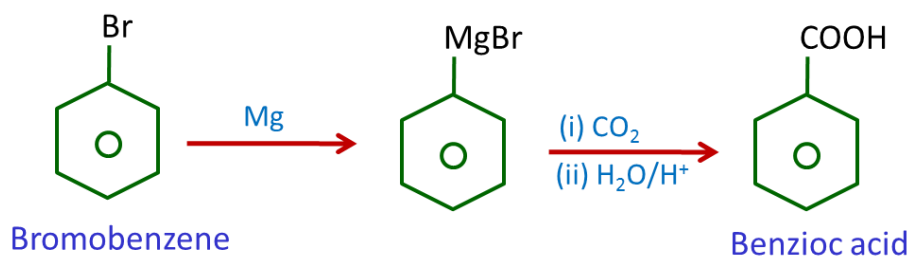
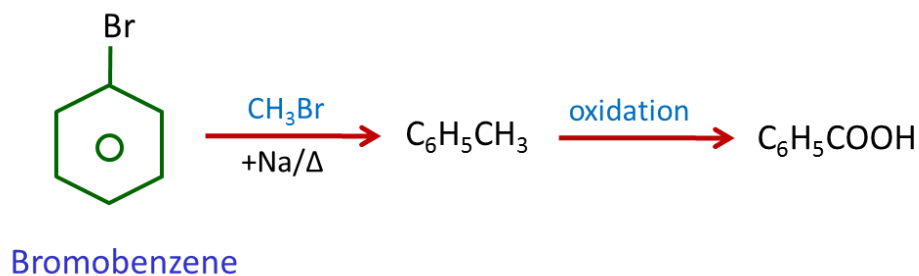
3. How will you synthesise benzyl alcohol from bromobenzene?

Solution:



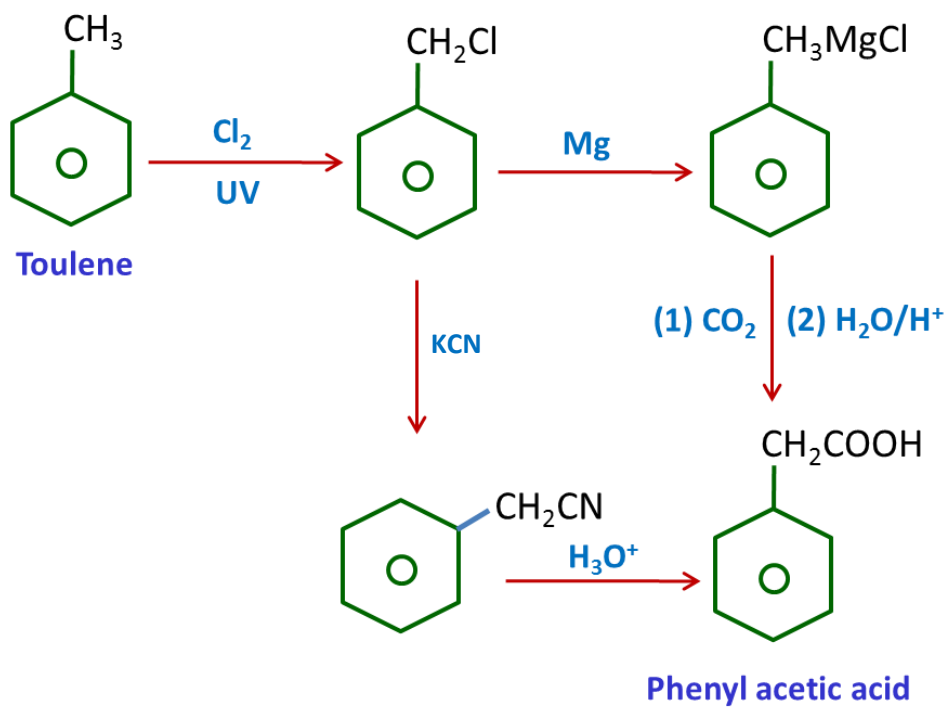
4. How will you synthesise benzoic acid from bromobenzene?

Solution:



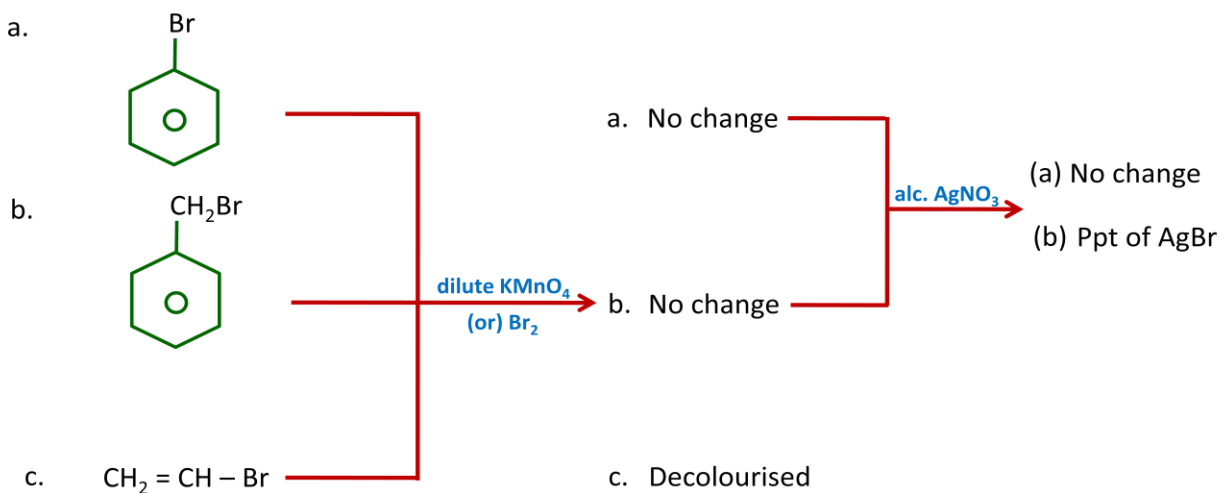
5. How will you synthesise phenylacetic acid from toluene?

Solution:



6. Using simple chemical tests, how could you distinguish between the following compounds?
- Bromobenzene
 - Benzyl chloride
 - Vinyl bromide

Solution:



7. What are the different isomers represented by the molecular formula C_7H_7Cl ?
Distinguish from one another?

Solution:

The isomers are:

