

10. Halogen Derivatives Of Alkanes & Arenes

	GSB/NCERT	MHT –CET	NEET	JEE Main
Haloalkanes				
➤ Introduction	GSB	✓	✓	✗
➤ Classification	GSB	✓	✓	✗
➤ Monohalogen derivatives	GSB	✓	✓	✗
➤ Nomenclature of alkyl halides	GSB	✓	✓	✓
➤ Nature of C–X bond in alkyl halides	GSB	✓	✓	✓
➤ Preparation	GSB	✓	✓	✓
➤ Physical properties and chemical reactions	GSB	✓	✓	✓
➤ Nucleophilic substitution mechanism	GSB	✓	✓	✓
Haloarenes:				
➤ Classification and Nomenclature.	GSB	✓	✓	✓
➤ Nature of C–X bond	GSB	✓	✓	✓
➤ Preparation	GSB	✓	✓	✓
➤ Substitution reactions (nucleophilic and electrophilic) Monosubstituted compounds only	GSB	✓	✓	✓
➤ Chemical reactions	GSB	✓	✓	✓
➤ Uses of some alkyl and aryl halides	GSB	✓	✓	✓
➤ Environmental effects of some alkyl and aryl halides	GSB	✓	✓	✓ (Only Chloroform and iodoform)

Halogen Derivatives Of Alkanes And Arenes

INDEX

	Topic Name	Page No.
01.	How to study Chapter ?	10.0.1 – 10.0.2
02.	Halogen Derivatives Of Alkanes And Arenes (<i>Additional points: Left Side</i>)	10.a.1 – 10.a.50
03.	Halogen Derivatives Of Alkanes And Arenes (<i>HSC Notes: Right Side</i>)	10.b.1 – 10.b.50
03.	Flow Charts	10.51 –10.52
04.	Additional Information	10.53 –10.57
05.	Intext Questions And Answers (GSB and NCERT)	10.58 – 10.70
06.	Past Board Exam Questions	10.71 – 10.72
07.	Theory Question bank given by Board	10.73 – 10.76

How to study Halogen Derivatives of Alkanes and Arenes

- 1) During lectures, write minimum and understand the reactions from printed notes.
During lectures, analyse
 - i) Change in functional groups
 - ii) increase (ascent) or decrease (descent) in carbon atom
 - iii) Types of reagents involved (remember the typical properties of reagents.)
 - iv) Type of reactions involved
 - v) Intermediate involved
- 2) When chapter is going on, solve MCQs from MCQ books like Internal MCQ book.
- 3) After every lecture, **read related taught part in fast mode**. Time for studying per page should be less than 3 min. Write and practice the reactions 2-3 times.
- 4) When 4 lectures are done, **solve internal MCQ book**. Before solving MCQ's, always write and **practice flow charts of reactions**
- 5) By the time, the chapter is almost done, finish solving all MCQ's from internal MCQ's books (all levels).
- 6) **Important Topics are:**
 - i) S_N^1 and S_N^2 mechanism
 - ii) Hydride and methyl shift
 - iii) R, S - system
 - iv) Optical isomerism
 - v) Name reactions
 - vi) E_1 and E_2 (Will be found in Supplement)
- 7) After solving internal MCQ books, solve other MCQ books like GRB, NEET champion, Pradeep Publications
- 8) Read & develop your understanding by **learning Oral Q/Ans** of Haloalkanes and Haloarenes.
- 9) Take help of your chemistry friends/parents, and allow them to ask you oral Q/ans.
- 10) Refer flow charts of Haloalkanes and Haloarenes on regular basis.
- 11) Visualise flow-chart and attempt conversion questions.
- 12) Attempt **objective Q/ans** for better development of the chapter.
- 13) Get MCQ & assignment doubts cleared on regular basis during lecture sessions.

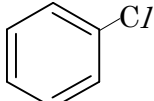
Intentionally Kept Blank

Clear Concept Tutorials
Clear Concept Tutorials

10. HALOGEN DERIVATIVES OF ALKANES AND ARENES

10.1 DEFINITION:

When one or more hydrogen atoms of alkane or arene are substituted by corresponding number of halogen atoms (such as chlorine, bromine or iodine), the resulting compounds are called halogen derivatives of alkanes or arenes.

e.g: CH_3Cl , CH_2Br_2 , CHI_3 , CCl_4 , 

10.2 CLASSIFICATION OF HALOGEN DERIVATIVES:

A) On the basis of number of Halogen atoms.

Halogen derivatives of alkanes are classified as Monohalogen derivatives and polyhalogen derivatives.

1] Monohalogen derivatives

When one hydrogen atom of alkanes is substituted by one halogen atom, the compounds formed are called as monohalogen derivatives of alkanes.

e.g. CH_3Cl (methyl chloride), $\text{CH}_3\text{CH}_2\text{Br}$ (ethyl bromide)

2] Polyhalogen derivatives

When more than one hydrogen atoms of alkanes are substituted by corresponding number of halogen atoms, the compounds formed are called polyhalogen derivatives of alkanes. On the basis of number of halogen atoms present in a molecule, polyhalogen derivatives are further classified as dihalogen derivatives trihalogen derivatives, tetrahalogen derivatives, etc.

a] Dihalogen derivatives

When two hydrogen atoms of alkanes are substituted by two halogen atoms, the compounds formed are called dihalogen derivatives of alkanes.

e.g. CH_2Cl_2 (methylene dichloride) $\text{C}_2\text{H}_4\text{Cl}_2$ (ethylene dichloride)

b] Trihalogen derivatives

When three hydrogen atoms of alkanes are substituted by three halogen atoms, the compounds formed are called trihalogen derivatives of alkanes

e.g. CHCl_3 (chloroform) CHI_3 (iodoform)

c] Tetrahalogen derivatives

When four hydrogen atoms of alkanes are substituted by four halogen atoms, the compound formed are called tetrahalogen derivatives of alkenes

e.g. CCl_4 (carbon tetrachloride), CF_4 (carbon tetrafluoride)

10.3 MONOHALOGEN DERIVATIVES OF ALKANE (ALKYL HALIDES)**Definition**

Monohalogen derivatives of alkanes are obtained by the **replacement** of one hydrogen atom of the alkane by a halogen atom are called **alkyl halides**.

They are represented in general as **R-X** where R- = alkyl group and X = Cl, Br, I.

General Molecular formula is **C_nH_{2n+1} X**.

B) ON THE BASIS OF THE TYPE OF HYBRIDISATION OF CARBON BONDED TO THE HALOGEN ATOM**CLASSIFICATION**

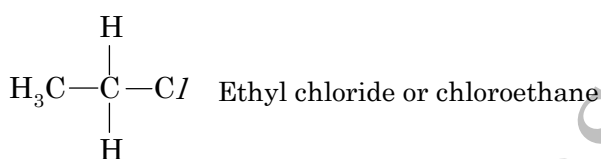
They are classified as:

1) Compounds containing sp³ C – X bond**A) Alkyl halides****i) Primary (1°) alkyl halide:** Alkyl halide in which the halogen atom is linked to a primary carbon atom

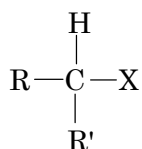
(i.e. 1° Carbon atom is the carbon which is attached to only one other carbon atom)

General Formula: **R-CH₂-X**

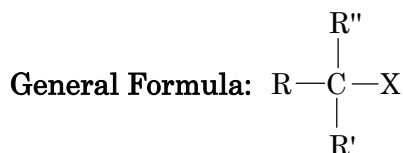
e.g.

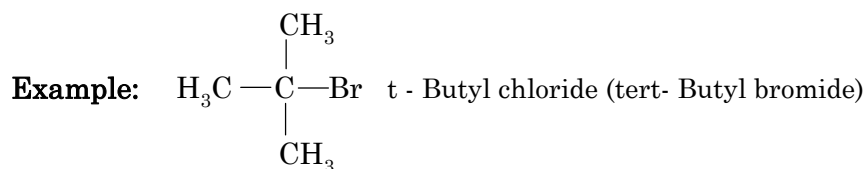
**ii) Secondary(2°) alkyl halide:** Alkyl halide in which the halogen atom is linked to a secondary carbon atom (i.e. 2° Carbon atom is the carbon which is attached to two other carbon atoms).

General Formula :



e.g.

**iii) Tertiary (3°) alkyl halide:** Alkyl halide in which the halogen atom is linked to a tertiary carbon atom (i.e. 3° carbon atom is the carbon which is attached to three other carbon atoms)



b) Allylic halides

These are the compounds in which the halogen atom is bonded to an sp^3 – hybridised carbon atom next to carbon – carbon double bond ($\text{C} = \text{C}$) i.e. to an allylic carbon.

General Formula:

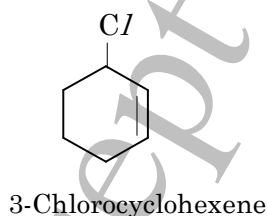


ii) Example:



Allyl bromide

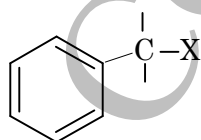
b)



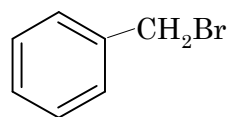
c) Benzylic halides:

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

General Formula:



Example:

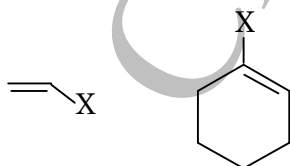


Benzyl bromide

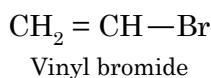
2) Compounds containing sp^2 C – X bond :

a) **Vinylic halides:** These are the compounds in which the atom is bonded to sp^2 – hybridised carbon atom of a carbon – carbon double bond i.e. vinylic carbon

General Formula:

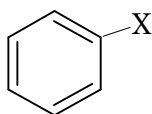


Example:

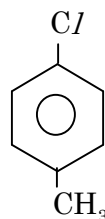


ii) **Aryl halides:** These are the compounds in which the halogen atom is bonded to sp^2 – hybridised carbon atom of an aromatic ring.

General Formula:



Example:

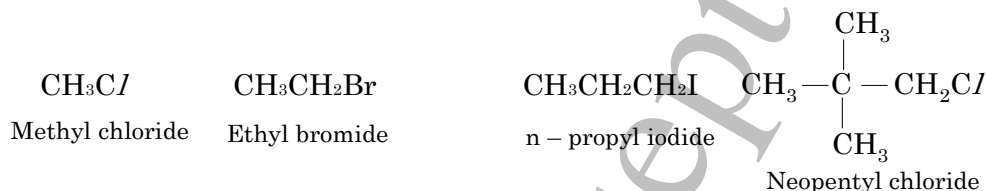


p-methyl chlorobenzene
(p-chlorotoluene)

10.4 NOMENCLATURE OF HALOALKANES:

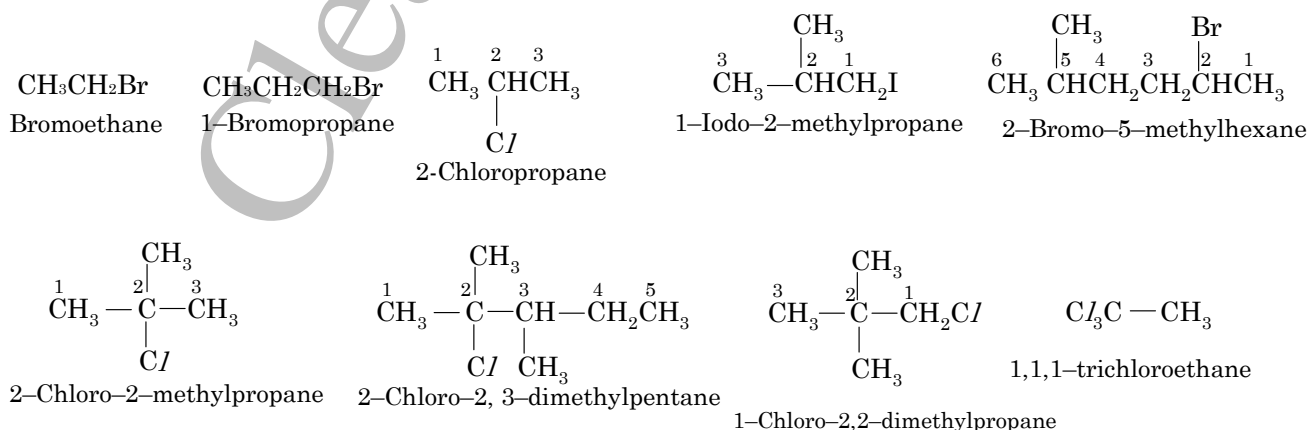
A) Mono halogen derivatives:

*In the common or trivial system, the mono halogen derivatives of alkanes are called **alkyl halides**.* These are named by naming the alkyl group attached to halogen and adding the name of the halide. For example,



In the IUPAC system, the monohalogen derivatives of alkanes are named as haloalkanes. The names are written by prefixing the word halo to the name of the alkane corresponding to longest continuous carbon chain holding the halogen atom. In case of branched chain alkanes, the following rules are followed:

- The longest continuous chain alkanes, the carbon attached to halogen group is selected as the **parent alkane**.
- The carbon atom is numbered in such a way that the carbon atom carrying the halogen atom gets the lowest number.
- The position of the halogen atom and other substituents (alkyl groups) are indicated by suitable numbers. i.e., 1, 2, 3,.... etc. Other common rules of alkanes are followed (see preview of organic chemistry). For example,



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

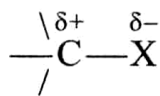
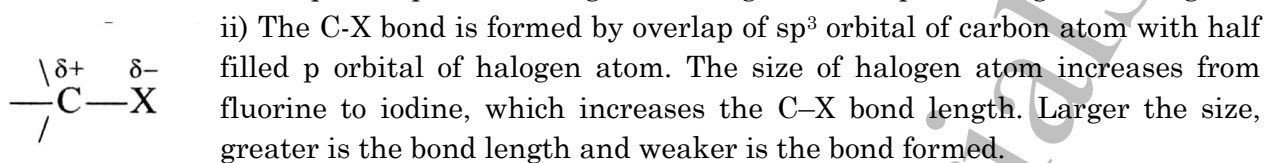
Alkyl halide	Common name	IUPAC name
CH_3Cl	Methyl chloride	Chloromethane
$\text{CH}_3\text{CH}_2\text{Br}$	Ethyl bromide	Bromoethane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{F}$	<i>n</i> – propyl fluoride	1 – Fluoropropane
$\begin{array}{c} \text{CH}_3 \text{ CHI} \\ \\ \text{CH}_3 \end{array}$	Isopropyl iodide	2 – Iodopropane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	<i>n</i> – Butyl chloride	1-Chlorobutane
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ \\ \text{Cl} \end{array}$	sec-butyl chloride	2-Chlorobutane
$\begin{array}{c} \text{CH}_3 \text{ CHCH}_2\text{Cl} \\ \\ \text{CH}_3 \end{array}$	Isobutyl chloride	1-Chloro-2-methylpropane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{Cl} \end{array}$	tert – Butyl chloride	2-Chloro-2-methylpropane
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2\text{CH}_2\text{Cl} \\ \\ \text{CH}_3 \end{array}$	Isopentyl chloride or Isoamyl chloride	1-Chloro-3-methylbutane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_2\text{CH}_3 \\ \\ \text{Cl} \end{array}$	tert – Pentyl chloride or tert – Amyl chloride	2-Chloro-2-methylbutane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_2\text{Cl} \\ \\ \text{CH}_3 \end{array}$	Neopentyl chloride or Neoamyl chloride	1-Chloro-2,2-dimethylpropane

NOTES:

Clear Concept Tutorials

10.5 NATURE OF C – X BOND IN ALKYL HALIDES :

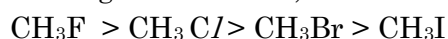
i) Carbon halogen bond is a polar bond as halogens are more electronegative than carbon. The carbon atom exhibits a partial positive charge and halogen atom a partial negative charge.



iii) Bond strength of C-X decreases from C–F to C–I in CH_3X . **Strongest bond is formed by overlap of orbitals of the same principle quantum number.**

Halogen	F	Cl	Br	I
Overlapping orbital	$2p_z$	$3p_z$	$4p_z$	$5p_z$

iv) The $2(sp^3)$ orbital of carbon cannot penetrate (while overlapping) into larger p orbitals (3^{rd} , 4^{th} and 5^{th} main energy levels) sufficiently to form strong bonds. Hence, the order of C-X bond strength in CH_3X is,

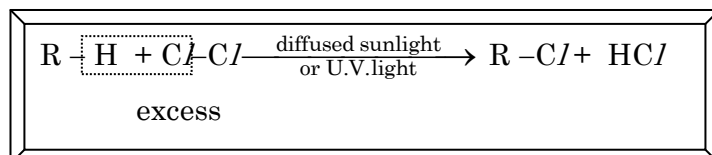


10.6 PREPARATION OF ALKYL HALIDES**1] From alkanes: By Halogenation**

The replacement of one or more hydrogen atoms of alkanes by halogens like Cl_2 , Br_2 , I_2 is called halogenation.

a. Chlorination:

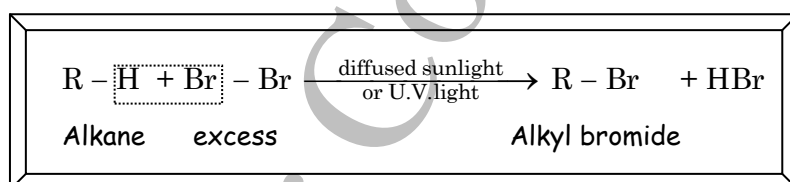
When alkanes are treated with excess of chlorine in the presence of *U.V. light or diffused sunlight or at high temperature*, it forms an alkyl chloride.



e.g.

b. Bromination:

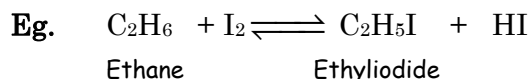
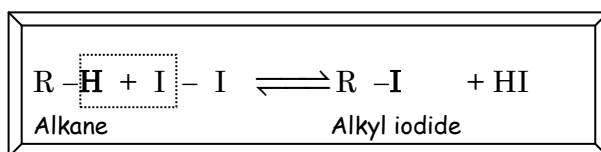
When alkanes are heated with excess bromine in the presence of UV light or diffused sunlight or at high temperature, it forms alkyl bromide.



e.g.

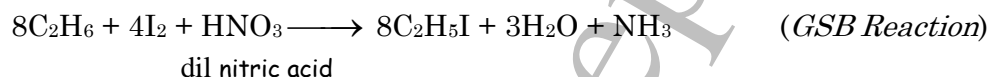
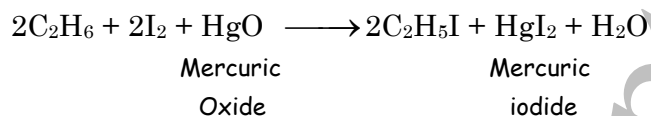
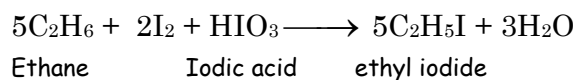
c. Iodination:

- i) When alkanes are treated with iodine, it forms alkyl iodide.



- ii) However, iodination reaction is a reversible reaction. Hydrogen iodide being a strong reducing agent reduces alkyl iodide back to alkane.
 iii) Thus the reaction needs to be carried out in presence of suitable oxidizing agent like mercuric oxide (HgO), iodic acid (HIO₃), dilute nitric acid (HNO₃), etc.

In the presence of an oxidizing agent:



Iodination usually stops at monoiodo stage.

d. Fluorination:

Reactions of alkanes with fluorine are explosive. Moreover, hydrogen fluoride is poisonous and corrosive. Hence, alkyl fluorides are not prepared by halogenation of alkanes.

2) From alkenes (Alkylenes): By Hydrohalogenation

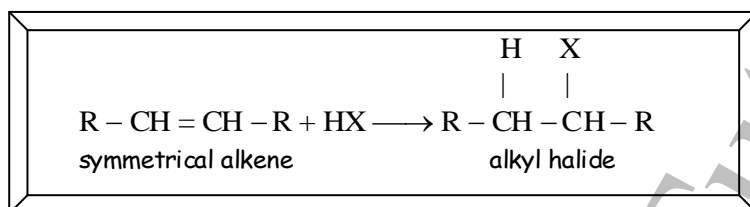
There are two types of alkenes:

a) Symmetrical alkenes like $\text{H}_2\text{C} = \text{CH}_2$ (Ethylene)

b) Unsymmetrical alkenes like $\text{H}_3\text{C} - \text{CH} = \text{CH}_2$ (propylene).

Alkenes readily react with halogen acids to give alkyl halides. The addition of halogen acid takes place across the double bond.

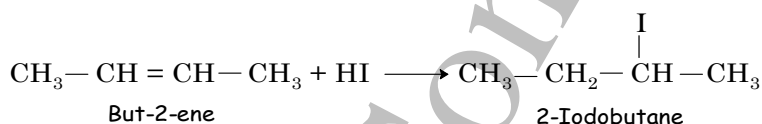
i. Hydrohalogenation of symmetrical alkenes:



e.g.

i)

ii)



Note: No rule applicable for above addition reaction

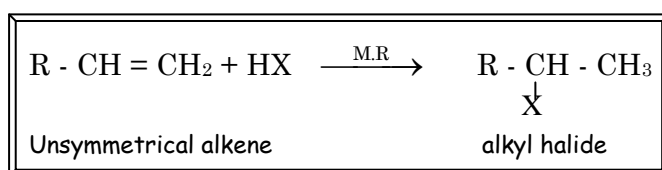
ii. Hydrohalogenation of unsymmetrical alkene:

The addition of hydrogen halide to an unsymmetrical alkene gives two products.

Propene on reaction with hydrogen bromide forms isopropyl bromide and n-propyl bromide

A) Markownikov's (Markownikoff's) Rule

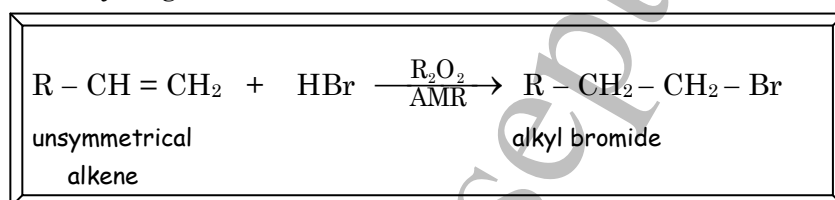
Statement: "When an unsymmetrical alkene (like propylene) is treated with unsymmetrical reagent (like HX), then the negative part of the reagent (X^-) gets added to that unsaturated carbon of the double bond, which contains lesser number of hydrogen atoms".



e.g.

B) Anti- Markownikov's (Anti-Markownikoff's) Rule (Peroxide effect) or Kharasch – Mayo effect

When an unsymmetrical alkene (such as propylene) is treated with unsymmetrical reagent (HX), in presence of peroxide such as R_2O_2 , the negative part of the reagent (X^-) gets added to that unsaturated carbon of the double bond which contains more number of hydrogen atoms.



e.g.

Note:

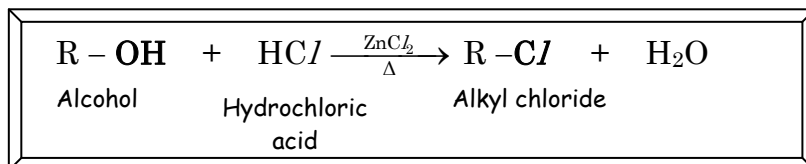
Peroxide effect is shown only by HBr, where as HCl and HI always add according to Markownikoff's rule.

3) From alcohol: Using Hydrogen halides, phosphorus halides (PX_3 , PCl_5) & Thionyl chloride ($SOCl_2$) :

i) Reaction with hydrogen halides:

a. With Hydrochloric acid (HCl):

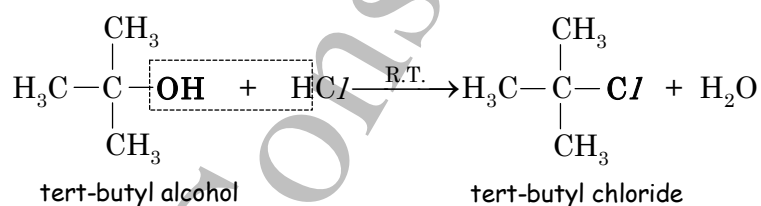
Alkyl chlorides are prepared by reacting alcohol with *Lucas reagent* (solution of concentrated hydrochloric acid with anhydrous zinc chloride).



e.g. i)

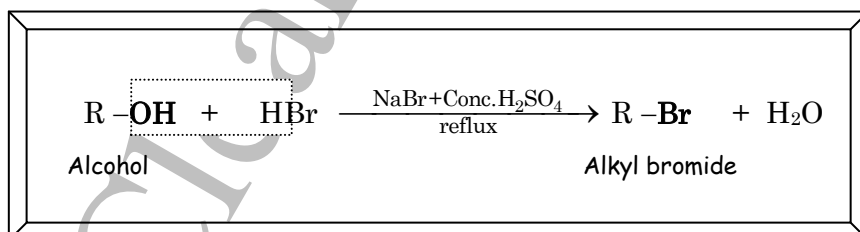
ii)

iii) With tertiary alcohols, the reaction is carried out by simply shaking with concentrated HCl at room temperature. (anhy. $ZnCl_2$ is not required for tertiary alcohols)



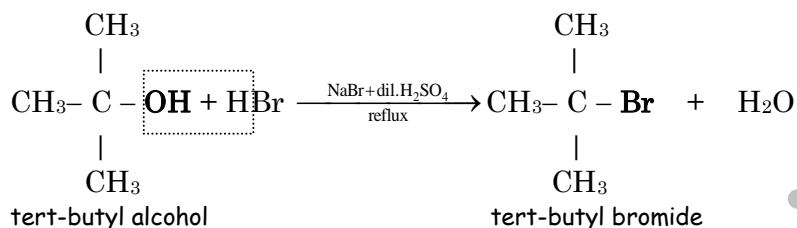
b. With hydrobromic acid (HBr): (Groove's process)

Alkyl bromides are prepared by refluxing suitable alcohol with hydrobromic acid. HBr being *corrosive* is prepared *in situ* by treating sodium bromide with concentrated sulphuric acid.



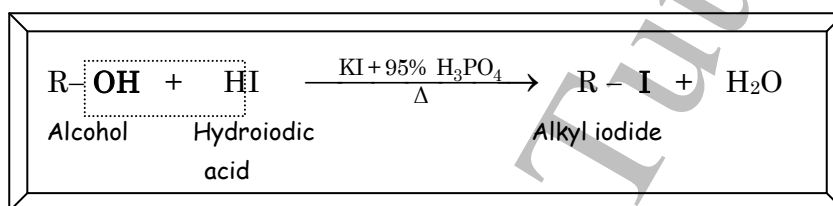
i. Ethyl alcohol on heating with concentrated hydrobromic acid forms ethyl bromide.

ii. Tertiary butyl alcohol on reaction with HBr forms tertiary butyl bromide.

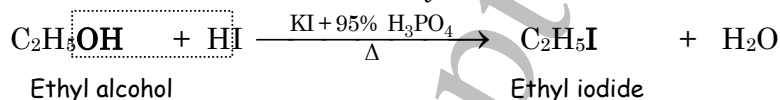


c. With hydroiodic acid (HI):

Alkyl iodides are prepared by heating alcohols with concentrated hydroiodic acid. HI being *corrosive* is prepared *in situ* by treating sodium or potassium iodide with 95% phosphoric acid



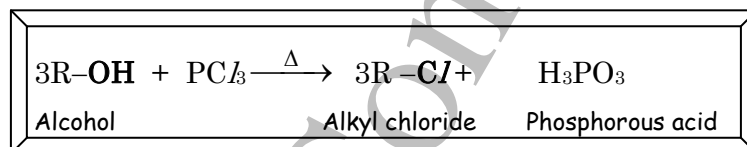
e.g. Ethyl alcohol on reaction with HI forms ethyl iodide.



(ii) Reaction with Phosphorus halides

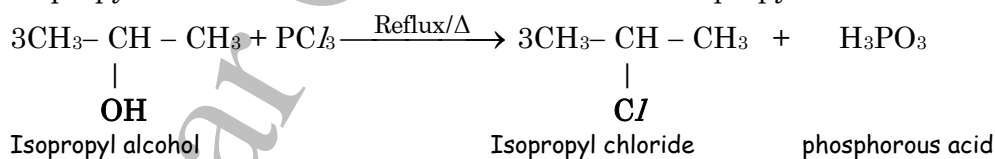
a. With phosphorus trichloride (PCl₃):

Alkyl chlorides are prepared by refluxing alcohols with phosphorus trichloride (PCl₃).



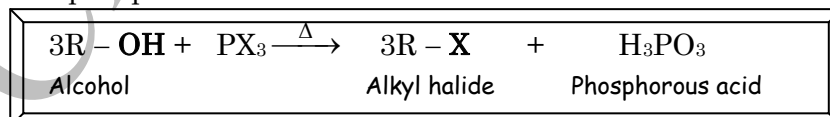
e.g.

i. Isopropyl alcohol when refluxed with PCl₃ forms Isopropyl chloride.



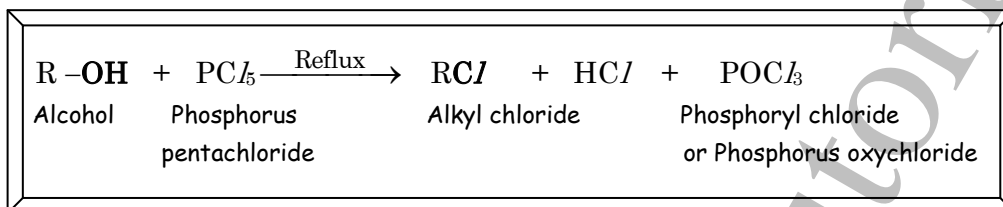
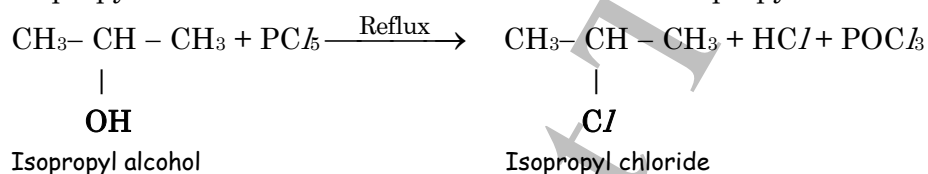
b. With phosphorus tribromide or phosphorus triiodide (PBr₃ or PI₃):

Alkyl bromides and alkyl iodides are prepared by the action of bromine or iodine in presence of red phosphorus on alcohols.



e.g. i.

ii.

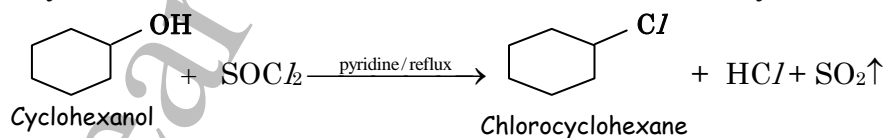
c. With phosphorus pentachloride (PCl₅):Alkyl chlorides are prepared by refluxing alcohols with phosphorus pentachloride (PCl₅).e.g. i. Isopropyl alcohol when refluxed with PCl₅ forms isopropyl chloride.**iii) With thionyl chloride or sulphonyl chloride (SOCl₂) (Darzen's method):**

Alcohols when refluxed with thionyl chloride, form alkyl chlorides.



e.g.

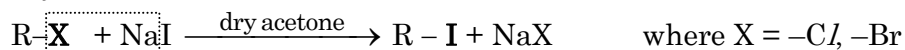
i.

ii. Cyclohexanol when refluxed with SOCl₂ forms chlorocyclohexane.

4) From alkyl halides: By Halogen exchange reactions

a. **Finkelstein reaction:**

Alkyl iodides are often prepared by the reaction of alkyl chlorides/bromides with NaI in dry acetone. This reaction is known as Finkelstein reaction.

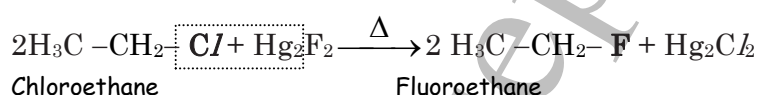
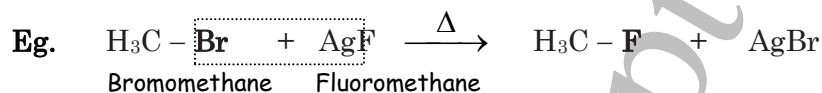


NaCl or NaBr thus formed is precipitated in dry acetone (& are easy to separate).

Eg

b. **Swart's reaction:**

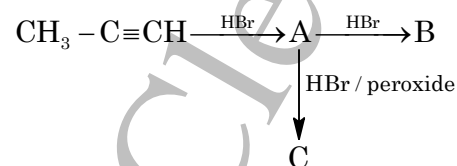
The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as AgF, Hg₂F₂, CoF₂ or SbF₃.



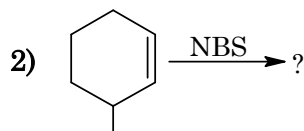
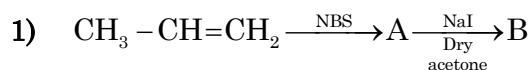
Convert :

1) 1-Butene to 1-Iodobutane

2)

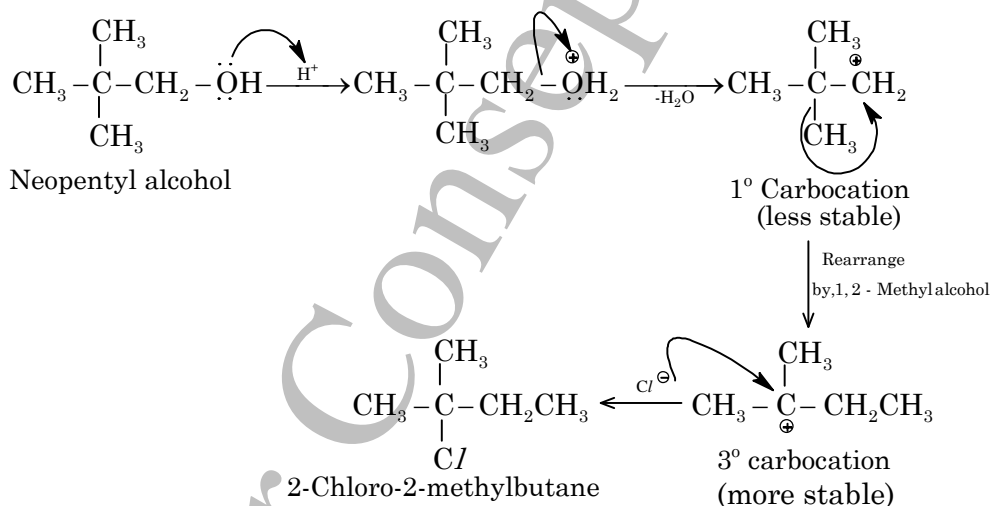


Convert :

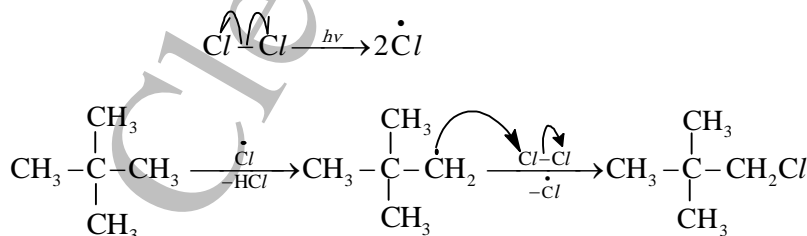
**Note:**

The best method to prepare Neopentyl chloride is by photochemical free radical chlorination of neopentane as compared to Neopentyl alcohol.

Because of the strong tendency of Neopentyl cation to rearrange to the more stable 3° carbocation, Neopentyl chloride cannot be prepared by the action of HCl on Neopentyl alcohol. Instead 2-chloro-2-methylbutane is



In contrast, free radicals normally do not rearrange. Therefore, the best method to prepare Neopentyl chloride is by photochemical free-radical chlorination of neopentane.



NOTES:

Clear Concept Tutorials

10.7 PHYSICAL PROPERTIES OF ALKYL HALIDE:

1) The lower members CH_3F , CH_3Cl , CH_3Br , $\text{C}_2\text{H}_5\text{Cl}$ and $\text{C}_2\text{H}_5\text{F}$ are gases at room temp.

2) Higher B.P. than parent alkanes.

Decreasing order of B.P. is : $\text{R} - \text{I} > \text{R} - \text{Br} > \text{R} - \text{Cl} > \text{R} - \text{F}$

among isomeric $\text{R} - \text{X}$, decreasing order of B.P. is = Primary > secondary > Tertiary

3) $\text{R} - \text{F}$ and $\text{R} - \text{Cl}$ \longrightarrow lighter than water

$\text{R} - \text{Br}$ and $\text{R} - \text{I}$ \longrightarrow heavier than water

Decreasing order of density is : $\text{R} - \text{I} > \text{R} - \text{Br} > \text{R} - \text{Cl} > \text{R} - \text{F}$

4) $\text{R} - \text{X}$ are polar co-valent compounds but insoluble in water because they cannot form H-bonds. They dissolve in organic solvents.

Clear Concept Tutorials

10. 8 CHEMICAL PROPERTIES OF ALKYL HALIDE:

Alkyl halides are very reactive & undergo variety of reactions.

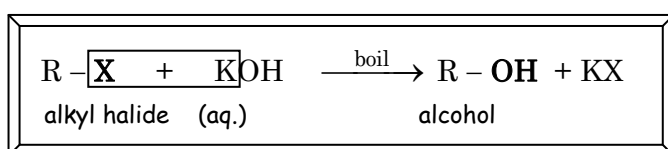
(A) SUBSTITUTION REACTIONS

In alkyl halides, the halide is easily replaced by many other functional groups.

Reactions in which an atom or group of atoms is substituted by another atom or a group of atoms respectively are known as Substitution reactions.

**1) Formation of alcohols : [-X \Rightarrow -OH (hydroxy)]****i. Reaction with aq. KOH or aq. NaOH (Hydrolysis of alkyl halides):**

Alkyl halides when boiled with aqueous alkali like KOH or NaOH undergo hydrolysis and form the corresponding alcohols. In this reaction, -X of R- X, is replaced by -OH group.



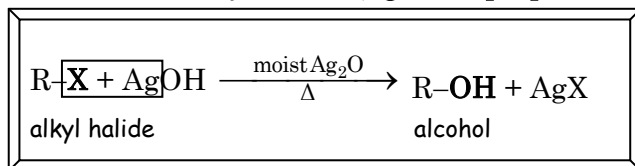
Eg.

i.

ii.

ii. Reaction with moist silver oxide:

Alkyl halides when boiled with moist silver oxide (Ag_2O), undergo hydrolysis and forms the corresponding alcohols. Since, silver hydroxide is less stable, silver oxide suspended in water behaves as silver hydroxide. (*AgOH is prepared in situ*)

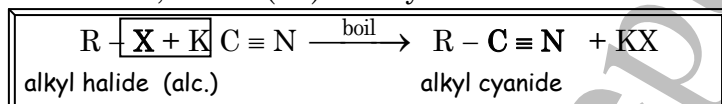


Eg.

2) Formation of alkyl cyanides or alkane nitriles: $[-\text{X} \Rightarrow -\text{C}\equiv\text{N} \text{ (cyano)}]$ Reaction with alc. KCN:

Alkyl halides (R-X) on boiling with alc. potassium cyanide, undergo substitution reaction to form the corresponding alkyl cyanides or alkane nitriles.

In this reaction, halide ($-\text{X}$) of alkyl halide is substituted by a cyanide group ($-\text{C}\equiv\text{N}$).



Eg. i.

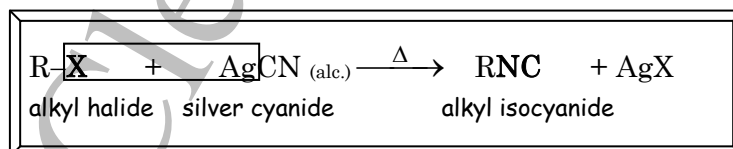
ii.

3) Formation of alkyl isocyanides or isonitriles or Carbylamine:

$[-\text{X} \Rightarrow -\text{N}\overset{\rightarrow}{\text{C}} \text{ (isocyano)}]$ Reaction with silver cyanide :

Alkyl halides when heated with silver cyanide forms alkyl isocyanide.

In this reaction, halide ($-\text{X}$) of alkyl halide is substituted by an isocyanide group ($-\text{NC}$).

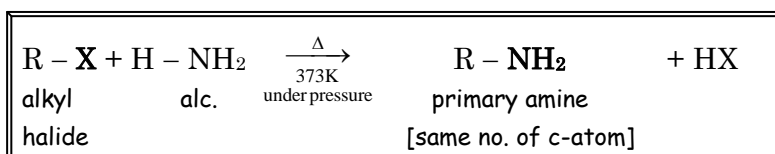


e.g.

4) Formation of Primary amines : Ammonolysis (Also known as Hoffmann Synthesis)

Reaction with alc. Ammonia [$-X \Rightarrow -NH_2$ (amino)]

Alkyl halides on boiling with **excess** of alcoholic solution of ammonia, under pressure, forms corresponding primary amines. This reaction is also known as **ammonolysis of alkyl halides**.



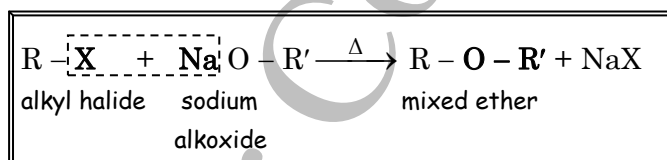
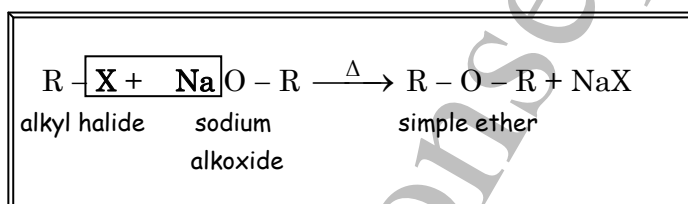
e.g.

i)

5) Formation of ethers (Williamson's synthesis) [$-X \Rightarrow -O - R$ (alkoxy)]

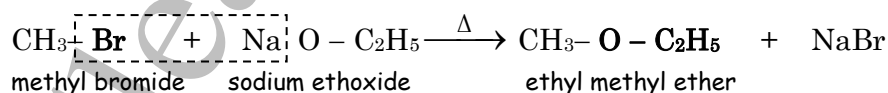
Reaction with sodium alkoxide :

Alkyl halides when boiled with sodium alkoxide undergo substitution reaction to form the corresponding ethers. In this reaction, halide ($-X$) of alkyl halides is substituted by an alkoxy group ($-O-R$). This reaction is known as **Williamson's synthesis** of ethers.



Eg.

i). Methyl bromide when boiled with sodium ethoxide undergoes substitution reaction and forms ethyl methyl ether.

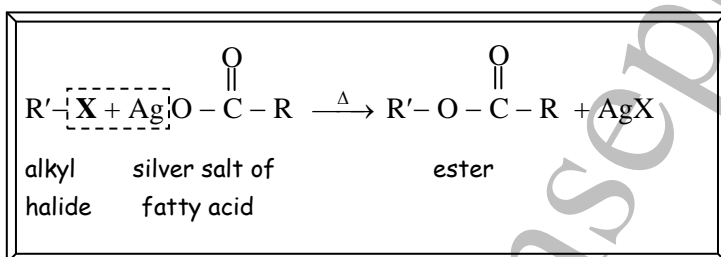


Limitations:

6) Formation of esters: [-X \Rightarrow RCOO - (carboxyloxy)]

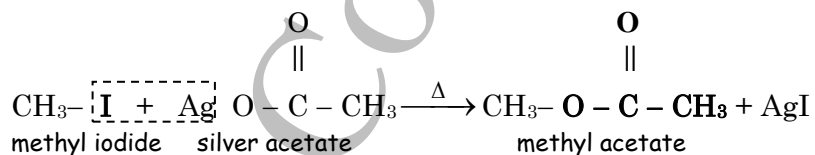
Reaction with silver salt of carboxylic acids:

Alkyl halides on heating with alcoholic solution of silver salt of carboxylic acid or fatty acids, get converted into corresponding esters. In this reaction, -X of R'-X is replaced by RCOO- group.



e.g.

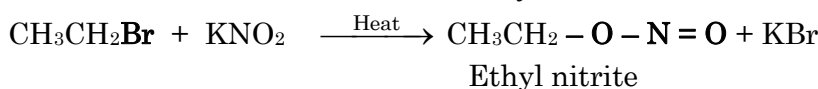
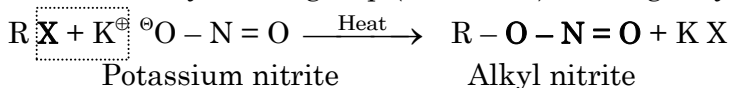
i) Methyl iodide on heating with silver acetate forms methyl acetate.



ii)

7) Substitution of halogen by nitrite group : (Formation of alkyl nitrites).

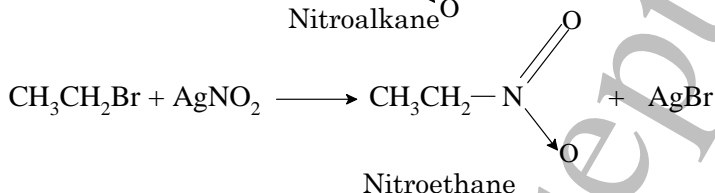
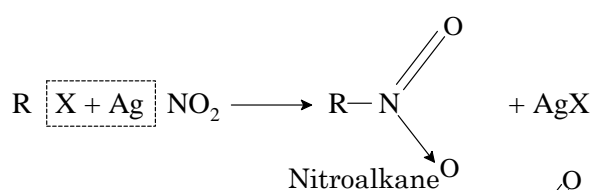
When a haloalkane is treated with sodium with potassium nitrite, the halogen atom gets substituted by nitrite group ($-O-N=O$) forming alkyl nitrites.



In KNO_2 (alkyl nitrites) the bond between $K-O$ is ionic and therefore, the negative charge on oxygen is the attacking site and therefore, forms alkyl nitrites ($R-O-N=O$).

8) Substitution of halogen by nitro group : (Formation of nitroalkanes)

When haloalkanes is treated with silver nitrite ($AgNO_2$), the halogen atom by nitro group ($-NO_2$) to give nitroalkanes.



In $AgNO_2$, the bond between $Ag-O$ is covalent and therefore, the nucleophile attack occurs through the lone pair on nitrogen and therefore, forms nitroalkanes ($R-NO_2$).

9) Substitution by hydrogen or reduction:

Primary and secondary alkyl halides are readily reduced to alkanes by lithium aluminium hydride ($LiAlH_4$) which is a **hydride donor**.



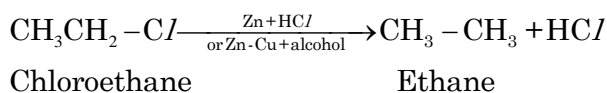
(From $LiAlH_4$)

Tertiary alkyl halides, however, undergo dehydrogenation to give alkenes. On the other hand, sodium borohydride ($NaBH_4$) reduces secondary and tertiary alkyl halides but not primary whereas triphenyltin hydride (Ph_3SnH) reduces all the three types of alkyl halides.

Reduction: Haloalkanes are reduced to the corresponding alkanes. This reduction is called hydrogenolysis and can be done by any of the following reagents:

Hydrogen in the presence of a metal catalyst such as nickel or palladium or platinum.

By the action of zinc or tin on hydrochloric acid or by the action of zinc-copper couple on alcohol.



NOTES:

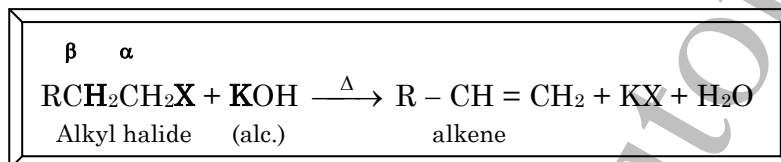
Clear Concept Tutorials

(B) ELIMINATION REACTION

The reaction in which two atoms or groups are removed from adjacent carbon atoms in a molecule to form an unsaturated compound like alkene is called elimination reaction.

1] Dehydrohalogenation reaction:

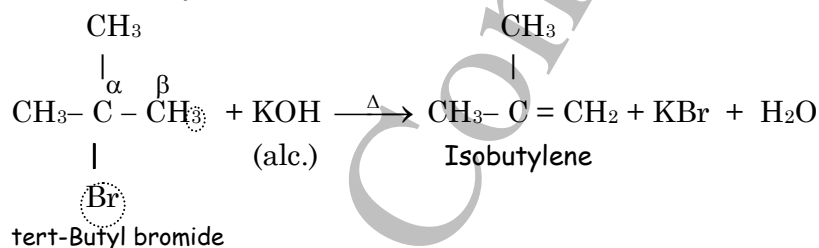
When a haloalkane with β -hydrogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from β -carbon and a halogen atom from the α -carbon atom. As a result, an alkene is formed as a product. Since β -hydrogen atom is involved in elimination, it is often called **β -elimination**.



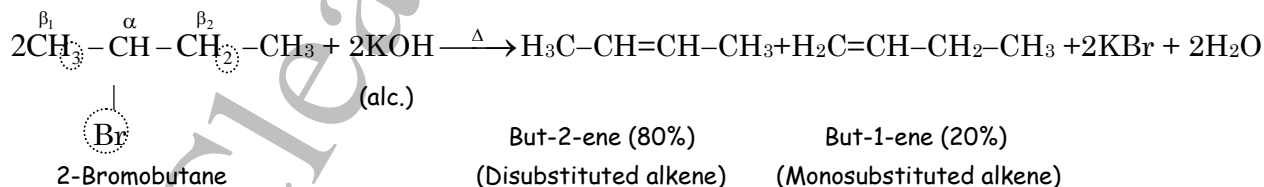
e.g.

i)

- ii) Tertiary butyl bromide when heated with alcoholic solution of potassium hydroxide forms Isobutylene.



- iii) Secondary butyl bromide when heated with alcoholic solution of potassium hydroxide forms But-2-ene (80%) and But-1-ene (20%) as per Saytzeff's rule.



There are two types of β hydrogens (β_1 & β_2) therefore two alkenes are expected.

Major product is decided by Zaitsev Rule (Saytzeff's Rule).

Saytzeff's rule: *If there is possibility of formation of more than one alkene due to the availability of more than one β -hydrogen atoms, usually one alkene is formed as the major product.*

Saytzeff's Rule: Poor carbon becomes poorer (i.e hydrogen is lost from carbon carrying lesser number of hydrogen atoms).

These form part of a pattern first observed by Russian chemist, **Alexander Zaitsev** (also pronounced & written as Saytzeff) who in 1875 formulated a rule which can be summarised as

“In dehydrohalogenation reactions, the preferred product is that alkene which has the greater

number of alkyl groups attached to the doubly bonded carbon atoms.”

The reactivity of haloalkanes towards elimination reaction. i.e., ease of dehydrohalogenation is in the order : **Tertiary > Secondary > Primary**

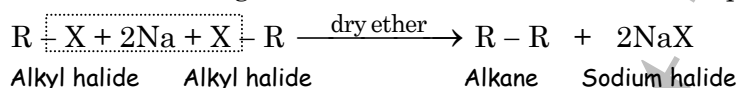
⇒ Refer comparison between substitution and elimination on page no. 10.a.31

(C) REACTION WITH METALS :

1) Reaction with sodium : Wurtz reaction (Formation of higher alkanes)

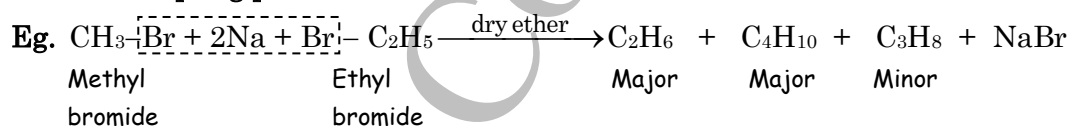
Ascent of Carbon

When an alkyl halide is treated with sodium metal in pure and dry ether, a hydrocarbon is formed containing twice the number of carbon atoms present in the alkyl halide.



e.g.

If mixture of two different alkyl halides is treated with sodium in presence of dry ether, a mixture of alkanes is obtained. **Self-coupling products are formed in preference to cross coupling products.**



(Ethane & n-butane in above reaction are self-coupling products, hence they are major products)

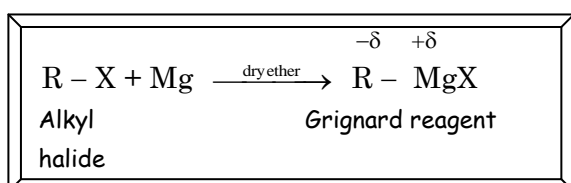
2) Reaction with magnesium: Formation of Grignard reagent

i. *Grignard reagent is an organometallic compound in which the divalent magnesium is directly linked to an alkyl group and a halogen atom.*

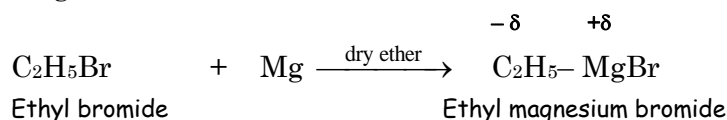
ii. General formula: R-MgX

iii. When a **dry** alkyl halide is treated with pure and **dry** divalent magnesium metal in presence of pure and dry ether, an alkyl magnesium halide (Grignard reagent) is obtained.

Since the Grignard reagent gets decomposed by moisture, **dry conditions** must be obtained.



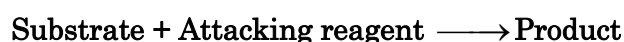
Eg. Ethyl bromide when treated with magnesium in presence of dry ether forms ethyl magnesium bromide.



- iv. In the Grignard reagent, carbon–magnesium bond is highly polar and magnesium–halogen bond is ionic in nature. $\left[\overset{\delta^-}{\text{R}}-\overset{\delta^+}{\text{Mg}}\text{X}^\ominus \right]$
- v. Grignard's reagent is highly reactive.
- vi. It reacts with numerous organic as well as inorganic compounds.
- vii. It is used in preparation of a large number of organic compounds.

10.9 TYPES OF REACTIONS:

Organic chemical reaction, in general, can be represented as:

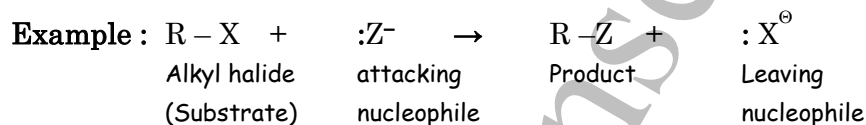


Therefore, depending upon the nature of the attacking reagent, organic reactions are mainly classified into three groups:

- i) Electrophilic reactions
- (ii) Nucleophilic reactions
- (iii) Free radical reactions.

10.9.1 NUCLEOPHILIC SUBSTITUTION REACTIONS:

Organic chemical reaction in which the attacking nucleophile (Z) replaces another nucleophile (X) to form the product is called a nucleophilic substitution reaction.



Depending upon the chemical kinetics (study of rate of reaction), nucleophilic substitution reactions are classified into two groups:

- i) First order – Nucleophilic substitution reaction.
- ii) Second order – Nucleophilic substitution reaction.

Important terms Involved:

a) Substitution reaction:

The reaction in which an atom *or* group of atoms is replaced by another atom or group of atoms is called substitution reaction.

b) First order nucleophilic substitution (S_N¹):

A type of nucleophilic substitution reaction in which the rate of reaction depend upon the concentration of the substrate *only* is called as first order nucleophilic substitution reaction.

c) Second order nucleophilic substitution (S_N²):

A type of nucleophilic substitution reaction in which the rate of reaction depend upon the concentration of both the substrate & reagent is known as second order nucleophilic substitution reaction.

d) Transition state:

The highly unstable state with maximum energy content which shows some resemblance with both the reactants and the products and *cannot be isolated* is known as transition state. It is denoted as T.S. (It involves partial bonds.)

e) Energy of activation:

The amount of energy that must be supplied to the reactants for the formation of transition state. It is denoted as ΔE or E_{act} .

OR

The difference between the energies of the transition state and that of reactants is known as energy of activation.

f) Threshold energy (enthalpy). The energy of transition state is known as threshold enthalpy (energy.)**g) Heat of reaction:**

The difference between the (energies) enthalpies of products and reactants is called heat of reaction.

$$\Delta H = H_P - H_R$$

Where H_R & H_P are (energies) enthalpies of reactants and products respectively

If $H_P > H_R$ then ΔH is positive and reaction is endothermic

(Products has more energy \Rightarrow less stable)

If $H_P < H_R$ then ΔH is negative and reaction is exothermic.

(Products has less energy \Rightarrow more stable.)

h) Energy profile diagram:

The graph obtained by plotting potential energy changes against rate of reaction is called energy profile diagram.

10.9.2 MECHANISM OF ALKALINE HYDROLYSIS OF METHYL BROMIDE**(S_N^2 REACTION):**

Consider the alkaline hydrolysis of methyl bromide with aq. KOH

a) Reaction :

Methyl attacking methyl leaving
bromide nucleophile alcohol nucleophile

Alkaline hydrolysis of methyl bromide follows S_N^2 mechanism

Where S = substitution, N = Nucleophilic, 2 = second order reaction

b) Kinetic expression:

Rate of reaction depends upon the concentration of both reactants. (*determined experimentally*)

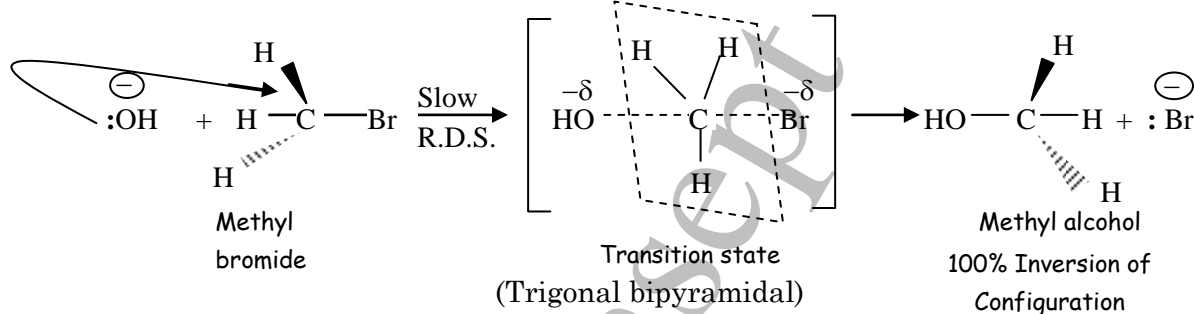
$$\text{Rate of reaction} \propto [\text{CH}_3\text{Br}][:\text{OH}^\ominus]$$

$$\text{Rate of reaction} = k [\text{CH}_3\text{Br}][:\text{OH}^-] \quad \text{where } k = \text{specific rate constant}$$

Since rate of reaction depends upon concentration of both the reactants i.e. substrate as well as reagent, it is *second order reaction*.

c) Mechanism:

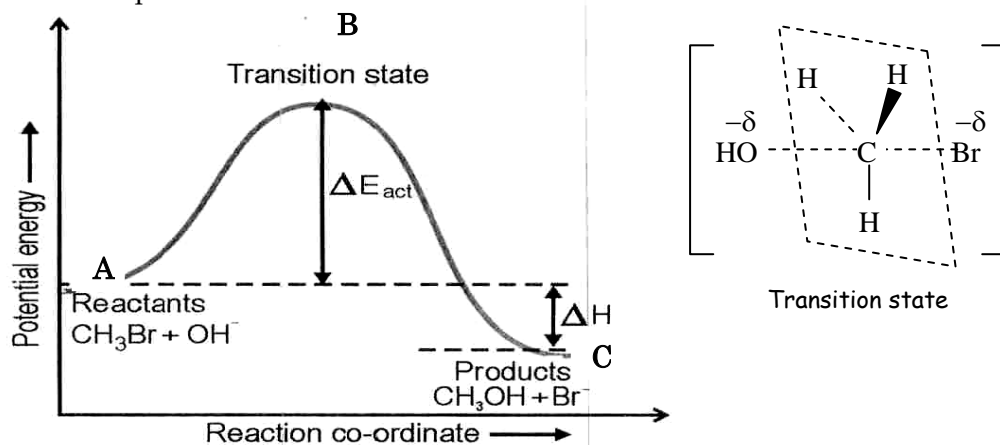
- This type of reaction occurs in **one step** through the formation of a transition state. In this mechanism, the nucleophile, OH^- attacks the partially positively charged carbon atom from the direction 180° away from the halogen atom.
- This leads to a transition state with a partially formed $\text{C}\cdots\text{OH}$ bond and a partially broken $\text{C}\cdots\text{Br}$ bond. This process is said to be a one step reaction. In the transition state, the negative charge is shared by both the incoming nucleophile as well as outgoing bromide.
- Hydroxide ion has diminished negative charge because it has begun to share its electrons with carbon while bromine has developed partial negative charge i.e., δ^- . The remaining three bonds to carbon in the transition state adopt a planar arrangement.
- This arrangement may be described as the C-H bonds are arranged like the spokes of a wheel with C-OH and C-Br bond lying along the axle, i.e. trigonal bipyramidal shape. The transition state is unstable because carbon atom is simultaneously bonded to five atoms and therefore, changes to products in which bromide ion leaves forming a C-OH bond. This reaction is shown below.



It is clear from the above one step mechanism, that the formation of transition state is rate determining step and therefore, the rate of the reaction depends upon the concentration of both alkyl halide and OH^- . Hence, it is a second order reaction.

d) Energy profile diagram:

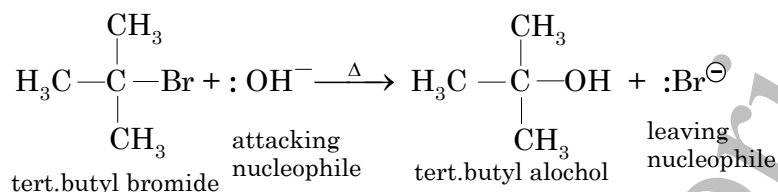
- It is a graph of potential energy changes during the reaction against rate of a reaction.
- The energy profile diagram for alkaline hydrolysis of methyl bromide which follows $\text{S}_{\text{N}}2$ mechanism is represented as follows:



Point A – Initial state	$\text{CH}_3-\text{Br} + :\text{OH}^\ominus$	$\Delta H =$ Heat of reaction (-ve \therefore exothermic)
Point B – transition state	$[\delta^-\text{HO}\cdots\text{CH}_3\cdots\text{Br}\delta^-]$	$\Delta E_{\text{act}} =$ Energy of activation
Point C – Final State	$\text{CH}_3-\text{OH} + :\text{Br}^\ominus$	

10.9.3 MECHANISM OF ALKALINE HYDROLYSIS OF tert – butyl bromide**(S_N¹ REACTION)**

Consider the alkaline hydrolysis of tertiary butyl bromide with aq. KOH.

a) Reaction:

Alkaline hydrolysis of tert – butyl bromide follows S_N¹ mechanism,
Where S = substitution, N = Nucleophile, 1 = first order reaction.

b) Kinetic expression:

i) Rate of reaction depends upon the concentration of (CH₃)₃C – Br only (determined experimentally)

ii) Rate of reaction \propto [(CH₃)₃C – Br]

\therefore Rate of reaction = $k[(\text{CH}_3)_3\text{C} - \text{Br}]$ where k = specific rate constant

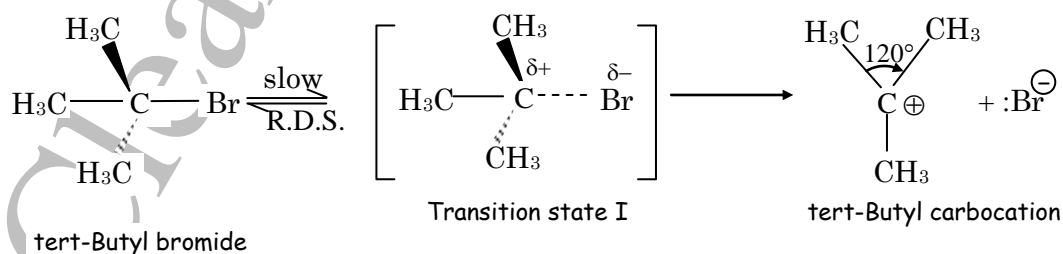
Since rate of reaction depends only upon the concentration of only substrate i.e. (CH₃)₃C – Br, it is First order reaction i.e. it follows first order kinetics.

c) Mechanism: *It is a two step reaction since breaking of C – Br & formation of C – OH takes place separately.***i. Formation of Carbocation:**

a) The C – Br bond in tert – butyl bromide is highly polar due to +I (positive inductive) effect of three methyl groups and –I (negative inductive) effect of bromine. As a result, in aqueous solution, the C – Br bond is slowly ionized to form a planar tert - butyl carbocation with bond angle of 120°.

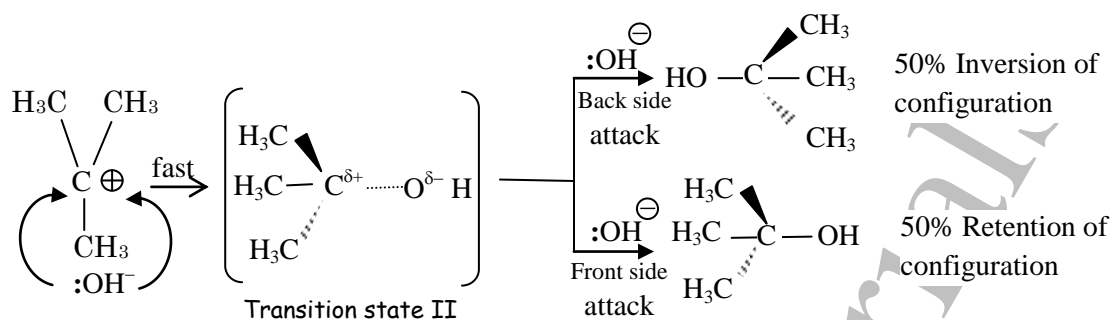
It is slow and reversible, hence rate determining step.

Energy required for breaking C – Br bond is obtained through solvation of halide ion with the proton of protic solvent.

**ii. Formation of the product:**

a) The positively charged carbocation can be attacked by hydroxide ion (nucleophile) from either side to give 50% retention and 50% inversion of configuration (racemization).

b) It is a fast process. The transition state decomposes fast by breaking the C – Br bond.



In S_N1 reactions, carbocations are the intermediates. Obviously, greater the stability of the carbocation, more easily it is formed and hence faster will be the rate of the reaction. Since the stability of carbocations decreases in the order:



therefore, reactivity of alkyl halides towards S_N1 reactions decreases in the same order. i.e., 3° alkyl halides $>$ 2° alkyl halides $>$ 1° alkyl halides $>$ methyl halides.

iii. Energy profile diagram:

Point A: Initial State $(\text{CH}_3)_3\text{C}-\text{Br} + :\text{OH}^\ominus$

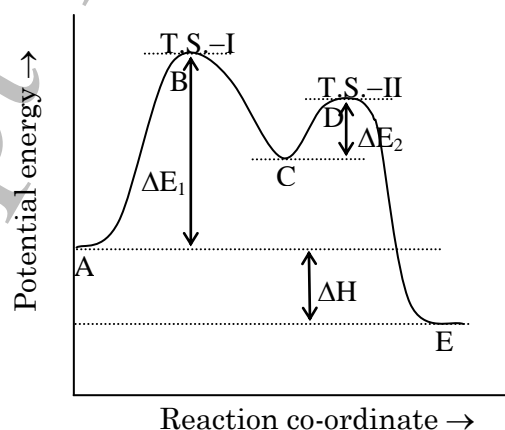
Point B: Transition state - I (T.S.-I)
 $[(\text{CH}_3)_3\text{C}^{\delta+} \cdots \text{Br}^{\delta-}]$

Point C: tert - butyl carbonium ion
 $(\text{CH}_3)_3\text{C}^+$

Point D: Transition state - II (T.S.-II)
 $[(\text{CH}_3)_3\text{C}^{\delta+} \cdots \text{OH}^{\delta-}]$

Point E: Final state
 $(\text{CH}_3)_3\text{C}-\text{OH} + :\text{Br}^\ominus$

ΔE_1 and ΔE_2 are energies of activation.
 ΔH = Heat of reaction.



NOTES:

Clear Concept Tutorials

NOTES:

Clear Concept Tutorials

10.10 OPTICAL ISOMERISM OF ALKYL HALIDES**i) Ordinary light:**

It consists of rays of different wavelengths, vibrating in all possible planes & perpendicular to the direction of propagation of light.

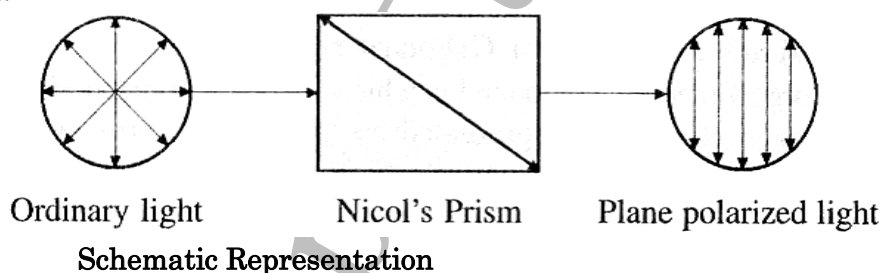
ii) Monochromatic beam of light:

It consists of rays of *single wave length* and they vibrate in different planes & perpendicular to the direction of propagation of light.

iii) Plane polarized light:

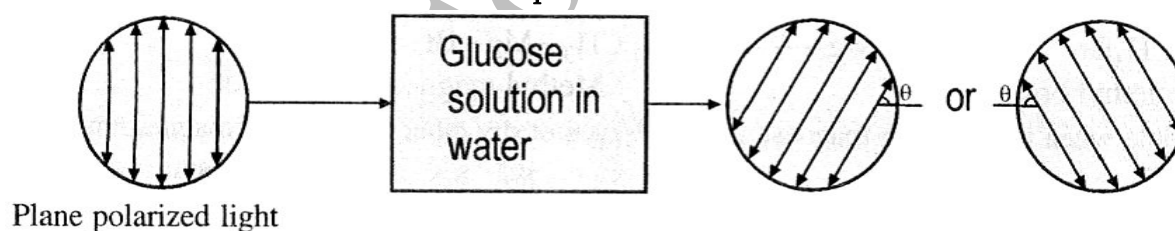
When a monochromatic beam of light is passed through *Nicol prism*, light obtained consists of rays of same wave length but they **vibrate in only one plane** which is perpendicular to the direction of propagation of light. This extra ordinary beam of light is called **plane polarized light**.

Schematic
Representation

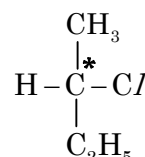
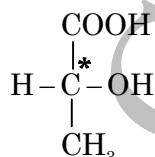
**iv) Optical Activity or Optical Isomerism:**

When a plane polarized light is passed through the aqueous solution of a substance (such as glucose, 2-butanol, lactic acid), it is observed that the plane of plane polarized light is rotated either to the right *or* to left. The substance is said to be chiral molecule (optically active molecule) & this property of the substance which rotates the plane of plane polarized light to the right or to the left is called **optical activity** or **optical isomerism**.

Schematic Representation



* Glucose is optically active (chiral) compound

v) Asymmetric Carbon (Chiral centre): A carbon atom which is attached to *four different* atoms or group of atoms is called chiral carbon atom or asymmetric carbon atom.

e.g Lactic acid

sec-butyl chloride (2-chlorobutane)

Above each compound has one asymmetric carbon atom (C*).

vi) **Dextro rotatory substance:**

The optically active substance which rotates the plane of plane polarized light to the right or clockwise is called a *dextro-rotatory substance*. It is denoted as *d* or (+).

e.g. d-glucose, (+)-lactic acid, d-2-chlorobutane.

vii) **Laevo rotatory substance:**

The optically active substance which rotates the plane of plane polarized light only to the left or anti clockwise is called a *laevo-rotatory substance*. It is denoted as *l* or (-).

e.g. l-fructose, (-)-lactic acid, l-2-chlorobutane.

viii) **Optical isomers:**

Organic compounds which have same molecular formula, same structural formula but different configuration (3-dimensional arrangement) around chiral centre (asymmetric carbon) are known as optical isomers. e.g. d-lactic acid & l-lactic acid are optical isomers.

Number of optical isomers (a) = 2^n

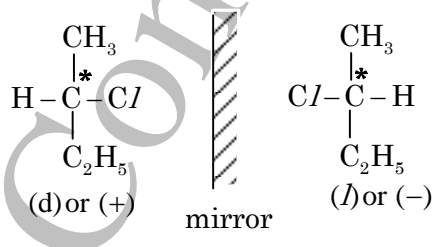
(n = No. of asymmetric carbon atoms or chiral centres)

ix) **Enantiomers:**

Pair of optical isomers which are **non-superimposable**, object-mirror images of each other are known as enantiomers. (They are also known as *enantiomorphs* or *optical anti-podes*)

*[common life example: pair of chappals.]

E.g. 2-Chlorobutane

x) **Racemic mixture or racemates :**

It is equimolar mixture of dextro & laevo forms of **same** optically active compound.

It is optically inactive due to **external compensation**. It is denoted by *d/l* or (\pm).

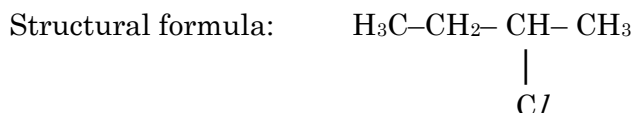
e.g. d/l-lactic acid, (\pm)-2-Chlorobutane

Racemic mixture can be resolved (separated) by the process called resolution.

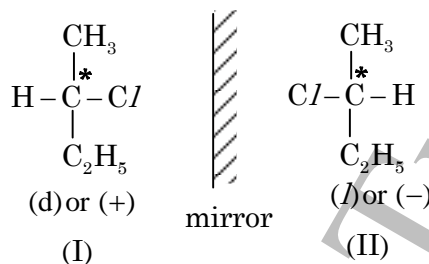
xi) **Chirality :**

A molecule containing asymmetric carbon atom would lack symmetry and is referred to as asymmetric molecule. This asymmetry of the molecule renders it **optically active**.

e.g. 2-Chlorobutane has chiral structure.

Optical isomerism of 2- Chlorobutane (sec-butyl chloride)

- 1) 2 - chlorobutane has one asymmetric carbon (chiral centre) attached to four different atoms or group of atoms viz. i) -H ii) -CH₃ iii) -C₂H₅ iv) - Cl
- 2) Number of possible optical isomers = $2^n = 2^1 = 2$ (n = number of asymmetric carbons)
- 3) Optical isomers of 2-chlorobutane:



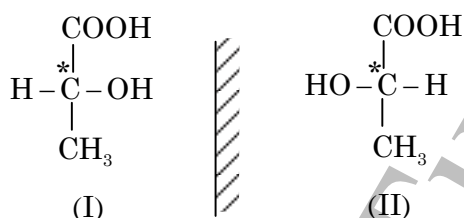
- 4) *If* Structure (I) rotates plane of plane polarized light towards right i.e clockwise direction, it is known as dextro-rotatory compound represented as d-2-chlorobutane or (+)-2-chlorobutane, then structure (II) rotates plane of plane polarized light towards left i.e anticlockwise direction, it is known as laevo-rotatory compound represented as *l*-2-chlorobutane or (-)-2-chlorobutane.

Above two structures are pair of **enantiomers**. These two optical isomers are the **non-super imposable** object mirror images of each other and rotate the plane polarized light by equal magnitude but in opposite direction.

- 5) Enantiomers have **similar** physical & chemical properties but **different** optical rotation.
- 6) A mixture containing **equimolar** proportion of the d and *l*-isomers (50% mixture of the enantiomers) of a substance is called a Racemic mixture. Racemic mixture is **optically inactive** due **external compensation**. It is denoted as (±)-2-chlorobutane or *d/l*-2-chlorobutane
- 7) Hence, 2- Chlorobutane exists in 3 forms:
 - (i) d - 2- Chlorobutane
 - (ii) *l*- 2- Chlorobutane
 - (iii) *d/l*- 2- Chlorobutane

Optical activity of lactic acidStructural formula: CH₃-CH-COOH

- 1) Lactic acid has one asymmetric carbon (chiral centre) attached to 4 different atoms or group of atoms viz. (i) – H (ii) – CH₃ (iii) – COOH (iv) – OH
- 2) Number of possible optical isomers = $2^n = 2^1 = 2$ (n = no. of asymmetric carbon atoms)
- 3) Optical isomers of lactic acid are:-



- 4) If structure (I) rotate the plane of plane polarized light toward right, i.e, clockwise direction, it is known as dextro rotatory compound represented as d- lactic acid or (+) – lactic acid; then structure (II) rotates the plane of plane polarized towards left, i.e, anticlockwise direction, it is known as laevo rotatory compound represented by l-lactic acid or (-) – lactic acid.

Above two structures are pairs of **enantiomers**. These two optical isomers are **non-super imposable mirror images** of each other and rotate the plane of plane polarized light by equal magnitude but in opposite direction.

- 5) Enantiomers have **similar** physical and chemical properties but **different** optical activation.
 - 6) A mixture containing equimolar proportion of the d and l-isomers (50% mixture of enantiomers) of a substance is called a **Racemic mixture**. Racemic mixture is optically inactive due to **external compensation**. It is denoted as (±) – lactic acid or d/l- lactic acid
- Hence, lactic acid exists in 3 forms:-

(i) d – lactic acid (ii) l- lactic acid (iii) d/l- lactic acid

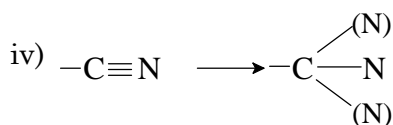
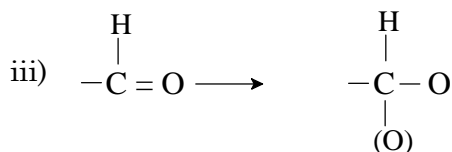
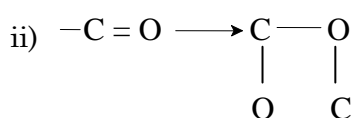
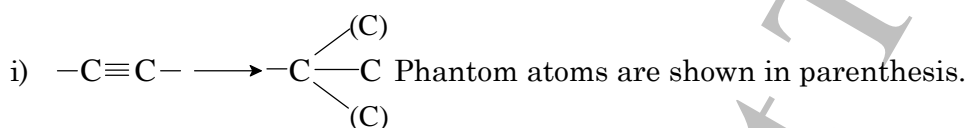
Absolute Configuration for Asymmetric Carbon atom (or Chiral Centre)**R, S configuration:**

The actual three dimensional arrangement of groups in a molecule containing asymmetric carbon is termed absolute configuration. The letter (R) comes from the latin **rectus** (means right) while (S) comes from the latin **sinister** (means left). It is better system because in many cases configuration to a compound cannot be assigned by d, l method.

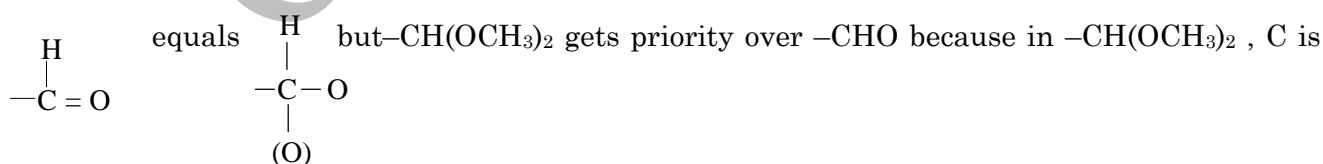
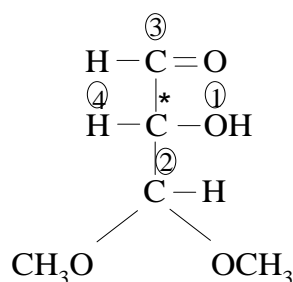
(R) and (S) nomenclature is assigned as follow:

- 1) This is a system of nomenclature which indicates the arrangements (configuration) of atoms around the chiral centre.
- 2) **Cahn-Ingold-Prelog system** or R, S convention is based on the priority of groups attached to chiral carbon atom.
- 3) Priority first assigned on the basis of the atomic number of the *atom that is directly attached to the chirality centre*.
- 4) The atom with **lowest atomic number** is given the **lowest priority**. The atom with next higher atomic number is given the next higher priority and so on, e.g. Oxygen has higher atomic number than carbon, hence oxygen is given higher priority.

- 5) If out of the four attached atoms in consideration, two are isotopic (like H and D), then priority goes to **higher atomic mass** i.e. D.
- 6) When a priority cannot be assigned on the basis of the atomic number of the *atom that is directly attached* to the chiral centre, then the next set of atoms in the unassigned group is examined.
- 7) We assign a priority at the first point of difference, e.g. the carbon atom in methyl group is attached to three hydrogen atoms (H, H, H) and the carbon atom in ethyl group is attached to one carbon and two hydrogen atoms (C, H, H). Carbon has higher atomic number than hydrogen.
Hence, Ethyl group is given higher priority than methyl group.
- 8) While deciding the priority, if the atom in consideration is attached further to an atom through a double bond then, it is treated as if it is attached to two such atoms. If the atom in consideration is attached further to an atom through triple bond then it is treated as if it is attached to three such atoms.

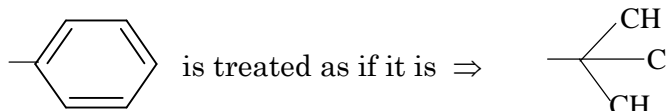


In the molecule



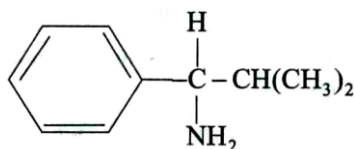
actually bonded to two oxygen atoms.

The phenyl group is



Out of $-\text{CH}_2-\text{CH}_3$ and $-\text{CH}=\text{CH}_2$; $-\text{CH}=\text{CH}_2$ gets priority.

In 1-amino-2-methyl-1-phenylpropane, the C,C,C of phenyl takes priority over C, C, H of isopropyl but not over N as it has a higher atomic number. The priority sequence is NH_2 , C_6H_5 , C_3H_7 , H.

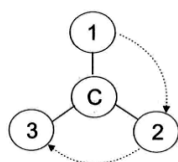


1-amino-2-methyl-1-phenylpropane

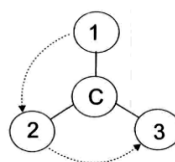
The order of priority as per C.I.P rule is: $\text{I} > \text{Br} > \text{Cl} > \text{SO}_3\text{H} > \text{F} > \text{OCOCH}_3 > \text{OH} > \text{NO}_2 > \text{NH}_2 > \text{COOCH}_3 > \text{COOH} > \text{CONH}_2 > \text{COCH}_3 > \text{CHO} > \text{CH}_2\text{OH} > \text{CN} > \text{C}_6\text{H}_5 > \text{C}_2\text{H}_5 > \text{CH}_3 > \text{D} > \text{H}$

R,S convention is based on the actual three-dimensional or tetrahedral structure of the molecule.

The molecule is viewed with the group of lowest priority behind the chiral carbon atom. If the clockwise arrangement of other three groups is in **descending** priority configuration is a designated '**R**'. If arrangement of groups is in anticlockwise direction, the configuration is designated as '**S**'.



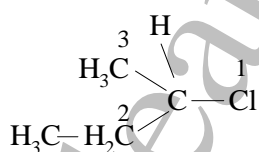
(R) Configuration



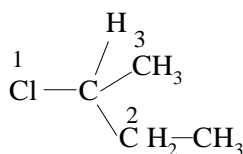
(S) Configuration

(The group of lowest priority is behind the chiral carbon atom)

e.g.



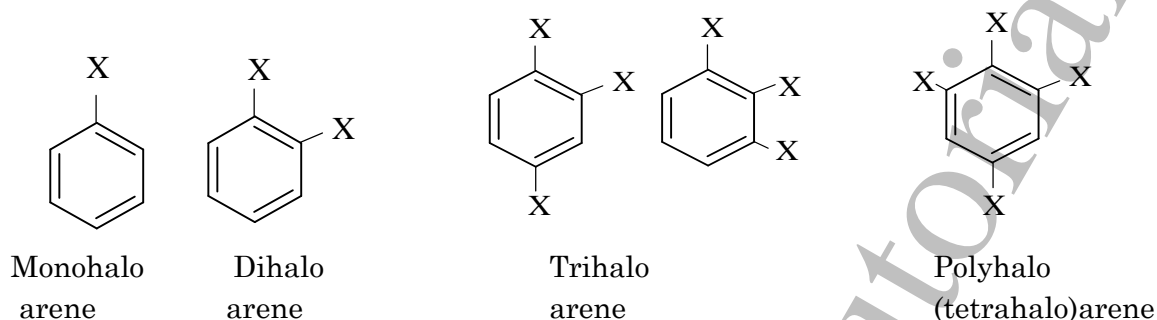
(R) -2- Chlorobutane



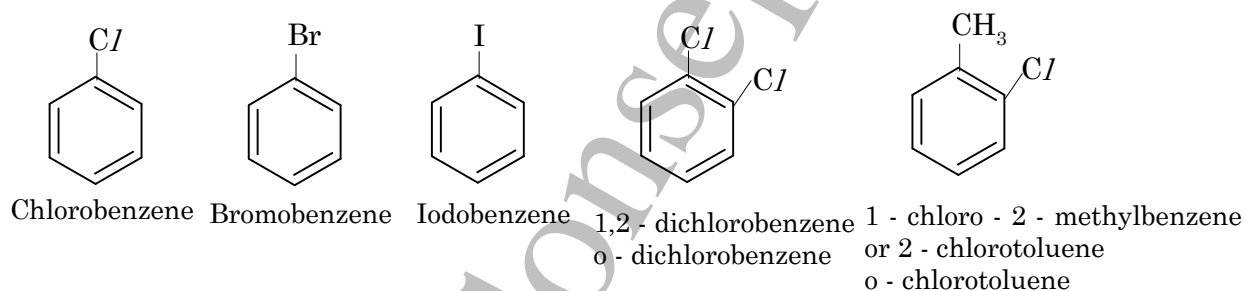
(S) -2- Chlorobutane

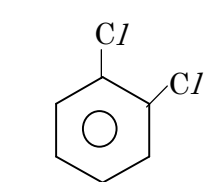
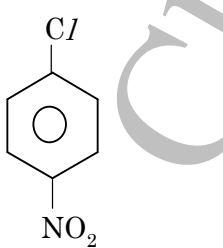
10.11 HALOARENES**10.11.1 Classification**

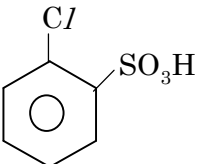
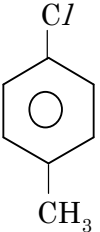
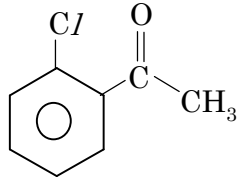
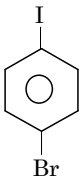
Haloarenes are classified as mono, di or polyhalogen compounds depending on whether they contain one, two or more halogen atoms in their molecules.

**Naming haloarenes (or aryl halides)**

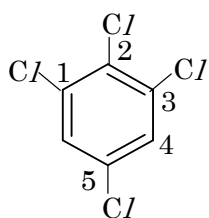
Haloarenes or aryl halides are named by adding the prefix halo (fluoro, chloro, bromo, iodo) before the name of the aromatic hydrocarbon. In case of disubstituted compounds, the relative positions of the substituents 1, 2 ; 1, 3 and 1, 4 are indicated by the prefixes ortho (o-), meta (m-) and para (p-) respectively. For example,

**10.11.2 Nomenclature :**

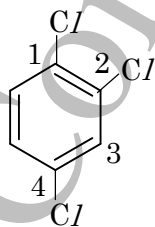
Structure	Common name	IUPAC name
	o-Dichlorobenzene	1,2-Dichlorobenzene
	p-Chloronitrobenzene	1-Chloro-4-nitrobenzene

	o-Chlorobenzenesulphonic acid	2-Chlorobenzenesulphonic acid
	p-Chlorotoluene	1-Chloro-4-methylbenzene (4-Chlorotoluene)
	o-Chloroacetophenone	2-Chloroacetophenone
	p-Bromoiodobenzene	1,4 - Bromoiodobenzene

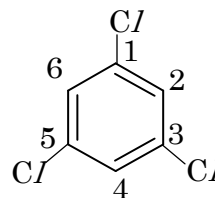
If more than two groups are attached to the benzene ring, numbers are used indicate their relative positions. (except three groups in symmetrical position, then sym. suffix is used)



1,2,3,5-Tetrachlorobenzene



1,2,4-Trichlorobenzene

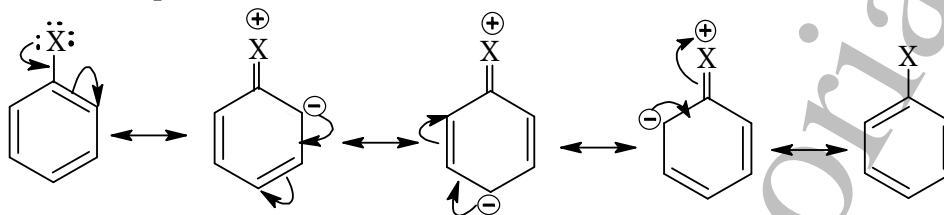


1,3,5-Trichlorobenzene

(Common Name: sym-trichlorobenzene)

10.11.3 NATURE OF C–X BOND IN HALOARENES:

- i. In haloarenes, the electron pair on halogen atom are in conjugation with π -electrons of the ring. The two electrons from lone pair of chlorine atom and 6 electrons from carbons of ring are associated to all the seven atoms (6 carbons and one halogen). The delocalization of these electrons gives **partial double bond character** to C–X bond.

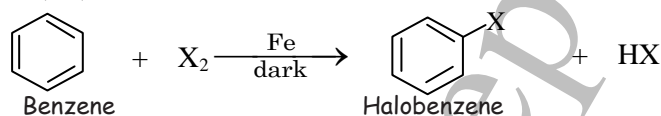


- ii. Due to **partial double bond character** of C–X bond in aryl halides, the C–X bond is **shorter** in length and stronger than in the alkyl halides.

10.12 PREPARATION OF HALOARENES:

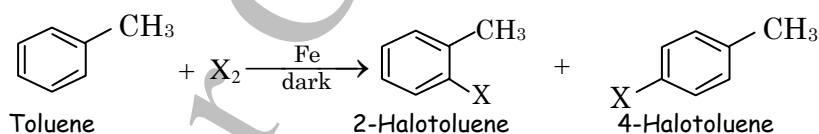
- i. **By electrophilic substitution reaction:**

- a. Aryl chlorides and bromides can be easily prepared by **electrophilic substitution** of arenes with chlorine and bromine respectively in the presence of **Lewis acid** catalysts like iron or iron(III) chloride i.e ferric chloride.



Eg.

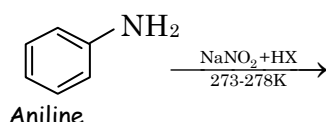
- b. In case of substituted benzene or arene, it gives ortho and para isomers. These isomers can be easily separated due to large difference in their melting points.

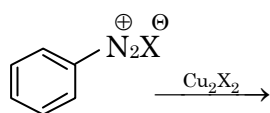


- c. Reactions with iodine are reversible in nature and require the presence of an oxidising agent (HNO₃, HIO₄) to oxidise the HI formed during iodination.
 d. Fluoro compounds are not prepared by this method due to high reactivity of fluorine.

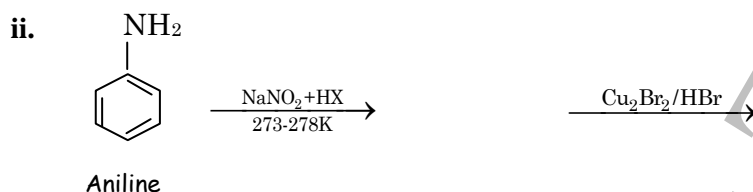
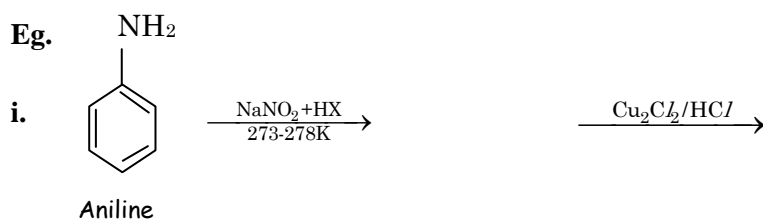
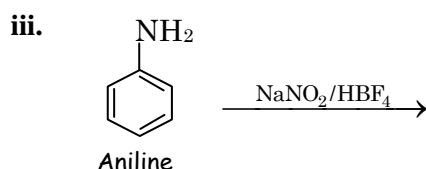
- ii. **By Sandmeyer's reaction: [Diazotisation]**

- a. When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed. Mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by –Cl or –Br

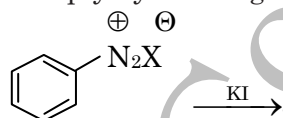




Eg.

**(Balz – Schiemann reaction)**

- b. Replacement of the diazonium group by iodine does not require the presence of cuprous halide and is done simply by shaking the diazonium salt with potassium iodide.

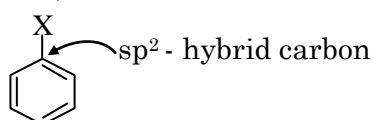
**10.13 SUBSTITUTION REACTIONS : (Monosubstituted compounds only)**

Substitutions reactions are of two types : Nucleophilic & electrophilic.

A) Nucleophilic substitution:

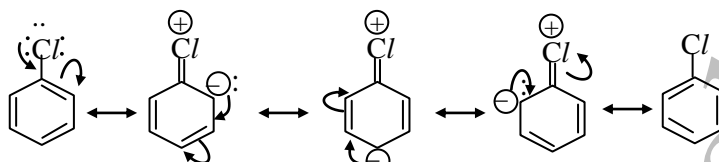
Under ordinary & normal conditions, aryl halides do not undergo nucleophilic substitution reactions. They are less reactive towards nucleophilic substitution due to following reasons :

- 1) In aryl halides, carbon of C-X bond is sp^2 hybridised, having more s-character & shorter bond length of 169 pm. Hence, greater energy is required to break the bond i.e **aryl halides are less reactive (than alkyl halides)**



[In alkyl halides, the carbon of C-X bond is sp^3 hybridised having less s-character & greater bond length of 177 pm, which requires less energy to break C-X bond i.e **alkyl halides are more reactive than aryl halides**]

- 2) In haloarenes, the lone pair of electrons of halogen atom are in conjugation with π -electrons of the aromatic ring.

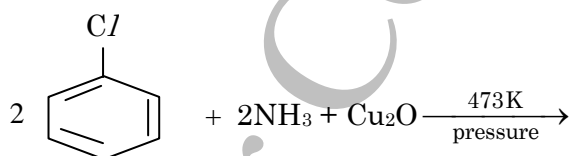
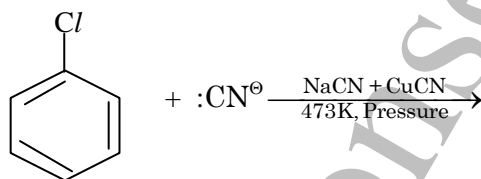
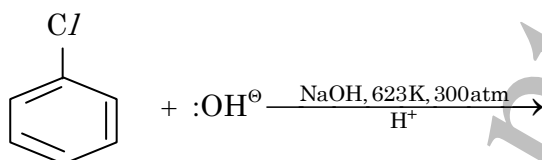


- 3) Due to the resonance, the C-X bond in aryl halides possesses partial double bond character.
 4) The phenyl cation produced due to the self-ionisation of haloarene is not stabilised by resonance which rules out the possibility of S_N1 mechanism. Even the back side attack of nucleophile is blocked by π -electrons of aromatic ring, which rules out S_N2 mechanism.
 Hence, aryl halides are less reactive than alkyl halides.

10.13.1 REACTIVITY OF ARYL HALIDES

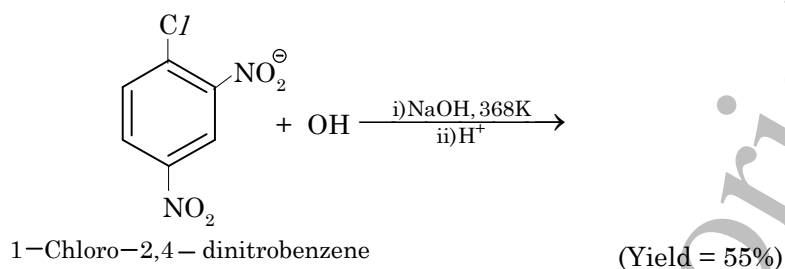
A] NUCLEOPHILIC SUBSTITUTION (-Cl/ replaced by other functional groups)

- 1) In aryl halides, -X group can be replaced by -OH, -CN or -NH₂ at higher temperature and under high pressure. (critical conditions).

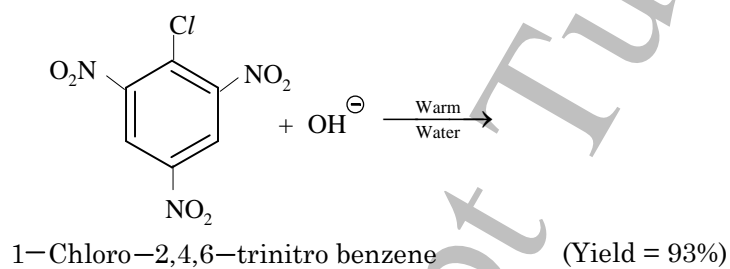


- 2) Aryl halides undergo nucleophilic displacement reactions ($-\text{Cl} \Rightarrow -\text{OH}$) readily if a strong electron withdrawing groups like $-\text{NO}_2$ is present at ortho or para positions.

- 3) Presence of electron withdrawing group at meta position has no effect on reactivity.
e.g. *2,4-dinitrochlorobenzene and 2,4,6-trinitro chlorobenzene reacts with the nucleophile OH⁻ to give the corresponding phenols.*



More electron withdrawing groups, greater is the reactivity.



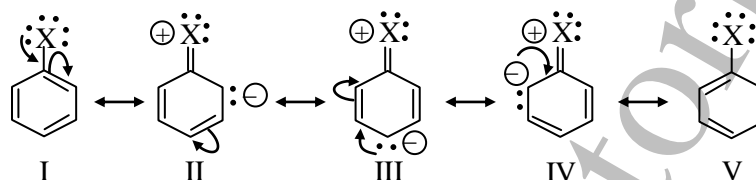
B) ELECTROPHILIC SUBSTITUTION (aromatic –H replaced by functional groups)

Aryl halides undergo electrophilic substitution reactions slowly. The halogen atom shows electron withdrawing inductive effect. It is o/p- directing and deactivates benzene ring.

(Conclusion: – X has –I effect & +M effect)

o/p-directing influence:

The o,p-directing influence of halogen atom can be understood by following resonating structures of halobenzene:



Due to resonance, the electron density increases more at ortho- and para-positions than at meta-positions.

Deactivating aromatic ring influence:

Halogen atom, because of its –I effect, has tendency to withdraw electrons from the benzene ring. As a result, the **ring gets deactivated** as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.

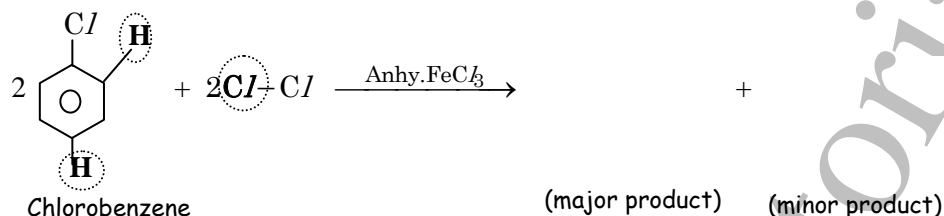
Conclusion: –X has strong –I effect and weak +M effect, hence it is deactivated aromatic compound.

10.13.2 CHEMICAL REACTIONS:

1) **Chlorination** : Introduction of chlorine in benzene ring.

Action of Cl_2 and anhy. FeCl_3 :

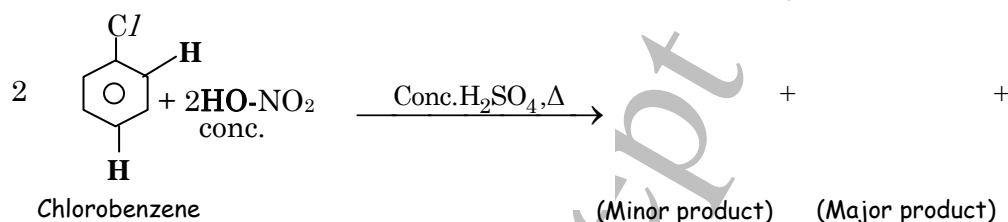
Chlorobenzene reacts with chlorine in the presence of anhydrous FeCl_3 to give ortho- and para-dichlorobenzene (major product).



2) **Nitration** : Introduction of nitro group ($-\text{NO}_2$) in benzene ring.

Action of conc. HNO_3 and conc. H_2SO_4 :

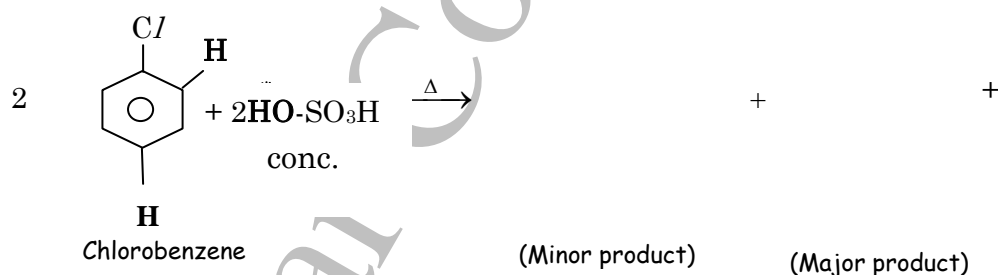
Chlorobenzene undergoes nitration at ortho- and para- positions to form chloronitrobenzene.



3) **Sulphonation** : Introduction of sulphonic acid group ($-\text{SO}_3\text{H}$) in benzene ring.

Action of hot conc. H_2SO_4 :

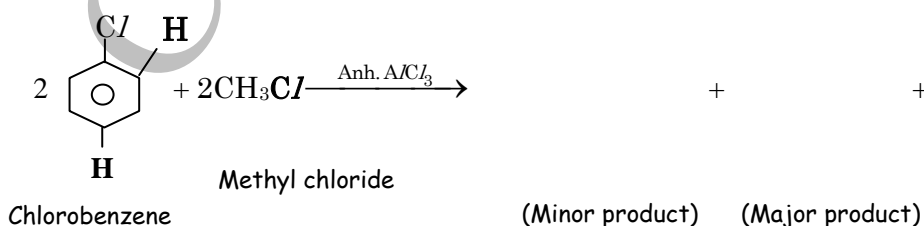
Chlorobenzene on treatment with conc. H_2SO_4 gives 2-Chlorobenzene sulphonic acid and 4-Chlorobenzene sulphonic acid (major product).



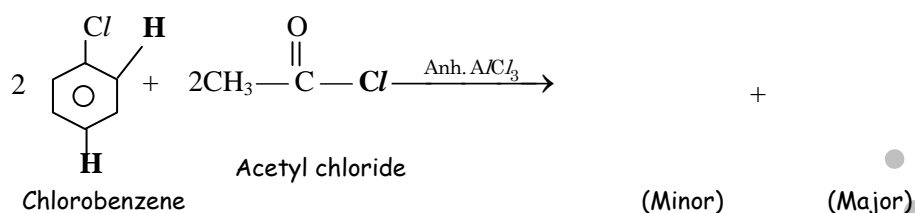
4) **Friedel-Craft's Reaction**

Chlorobenzene undergoes Friedel-Craft's reaction in the presence of anhydrous AlCl_3 .

a) **Friedel-Craft's alkylation** : Introduction of $-\text{R}$ (alkyl) in benzene ring.



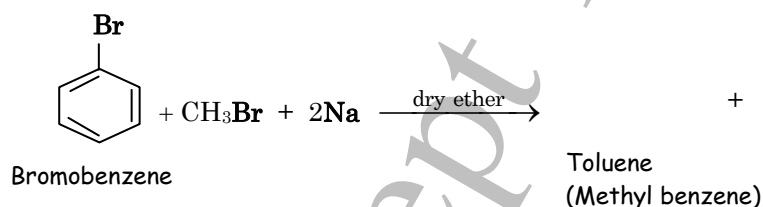
b) **Friedel-Craft's acylation** : Introduction of RCO– (acyl group) in benzene ring.



Chlorobenzene reacts with acetyl chloride in presence of anhy. aluminium chloride to form o-chloroacetophenone & p-acetophenone (major product)

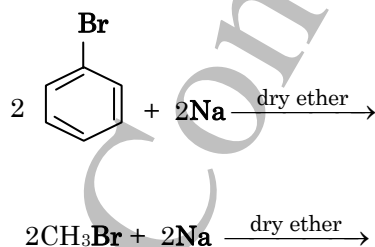
5) Reaction with sodium metal: *Wurtz-Fittig reaction*

Aryl halides react with alkyl halides and undergo ***coupling reaction*** when treated with sodium metal in presence of dry ether to form alkyl benzene. The reaction is known as **Wurtz-Fittig reaction**.

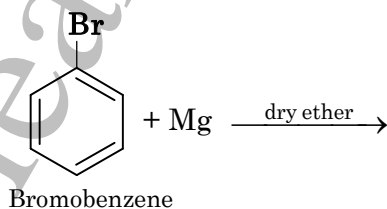


Fittig reaction

Other major products are self-coupling products – diphenyl, ethane as follows:



6) Reaction with Mg(Formation of Grignard's Reagent)



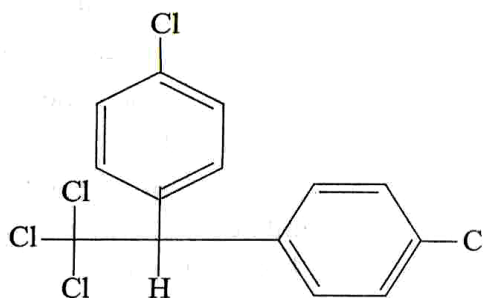
10.14 USES AND ENVIRONMENTAL EFFECTS OF SOME ALKYL & ARYL HALIDES

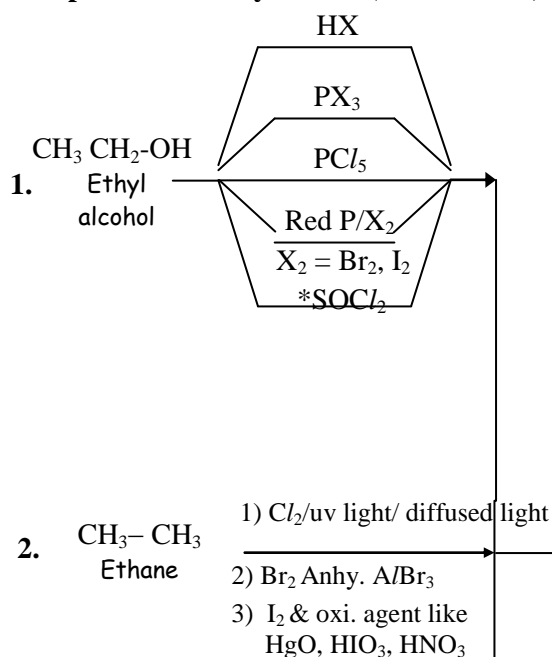
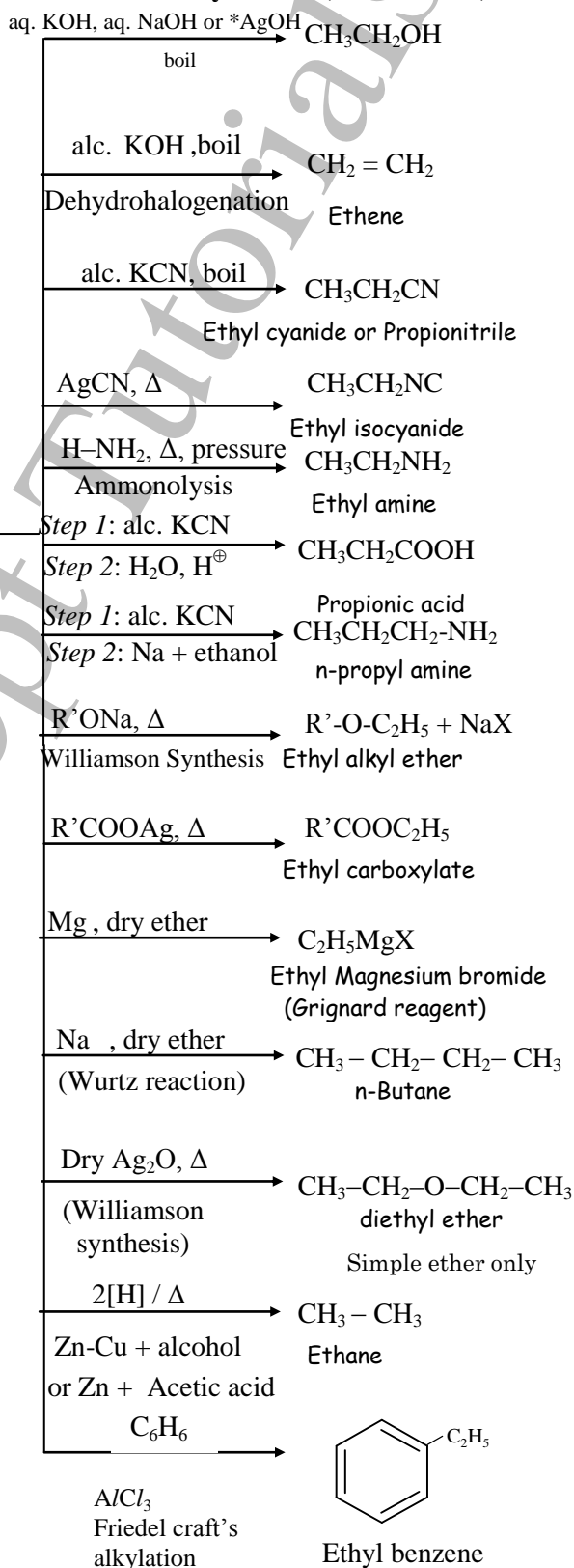
Sr No.	Compound	Uses	Environmental Effects
1)	Dichloromethane CH_2Cl_2 <u>Uses</u> (SDDPF) S= solvent D= Degreaser D= Decaffeinate P=Propellant F= Fumigant Env. Effects N ² VHE	1] To dissolve various organic compounds hence it is used as an ideal solvent. 2] As a degreaser and paint remover. 3] To decaffeinate tea and coffee. 4] Used as aerosol spray propellant as it is volatile 5] As a fumigant pesticide for grains and strawberries.	1] When mixed in air in high amount , as it highly volatile causes nausea , numbness in fingers and toes, dizziness if in less amount causes impaired vision and hearing . 2] It is highly dangerous if it comes in contact with eyes by damaging cornea.
2)	Trichloromethane or Chloroform CHCl_3 <u>Uses</u> (RSC) R= Refrigerant S= Solvent C= Carbene Env. Effects APHF	1] To prepare chloro-fluoromethane, a Freon refrigerant R-22. 2] As solvent in pharmaceutical industry and for producing pesticides and dyes. 3] As a source of dichloro Carbene ($:\text{CCl}_2$) group (e.g: Riemer-Tiemann Reaction).	1] Previously chloroform was used as anaesthetic but now it is replaced by ether due to its toxicity . 2] Chloroform when exposed to air and sunlight forms a poisonous compound, phosgene (carbonyl chloride, COCl_2), hence it is stored in dark, amber coloured, well stoppered bottles. 3] If mixed with air it is hazardous and causes headache and fatigue and if inhaled for long time affects central nervous system .
3)	Tetrachloromethane or carbon tetrachloride CCl_4 <u>Uses</u> (DPSR) D= Dry cleaning P= Pesticide S= Solvent Env. Effects EDVD ² O	1] As a dry cleaning agent 2] As a pesticide to kill insects in stored grains. 3] As a solvent 4] In the production of refrigerants .	1] On contact it causes eye irritation, damages nerve cells, vomiting sensation, dizziness , unconsciousness or death , thus it has severe adverse health effects. 2] When mixed with air it causes ozone depletion , which affects human skin leading to cancer.

4)	Iodoform: CHI₃ (Tri-iodomethane) Uses:(AD) A= Antiseptic D= Disinfectant	1] In medicine as a healing agent and <u>antiseptic</u> , dressing of wounds and sores. The <u>antiseptic</u> property is due to slow liberation of free iodine. 2] As <u>disinfectant</u> on small scale.	It has <u>strong</u> <u>smell</u> .
5)	Freons Uses (PFISFRA) P= Propellant F= Fire extinguishers I= Insecticides S=Solvent F=Forming agent R=Refrigerants A=Air conditioning	1] As <u>propellants</u> in Aerosol products of food, cosmetics and pharmaceutical industries. 2] Freons containing bromine in their molecules are used as <u>fire</u> extinguishers. 3] In aerosol <u>insecticides</u> . 4] As <u>asolvent</u> for cleaning clothes and metallic surfaces, 5]As <u>forming</u> agents in preparation of foamed plastics and in production of certain fluorocarbons. 4] As <u>refrigerants</u> 5]For <u>air</u> conditioning, as are noncorrosive.	1] As a refrigerant causes <u>ozone</u> depletion. 2]Most of the freons have low <u>toxicity</u> and low biological <u>activity</u> . 3]Freons from propane group are more toxic in nature. <i>Most widely used Freons are</i> <i>Dichloro difluoro methane</i> <i>CCl₂F₂</i> <i>Trichloro fluoro methane</i> <i>CCl₃F</i> <i>Chloro Difluoro methane</i> <i>CHClF₂</i>
5)	D.D.T: p, p-Dichloro diphenyl trichloro ethane	1]As insecticide against malaria. 2]To kill various insects like housefly and mosquitoes due to its high and specific toxicity.	1) It is not readily metabolized and not destroyed by environment. 2) It is deposited in fatty tissues. 3) If it exists for a long time in soil, plants and animals, it produces unforeseen ecological effects.

DDT (Dichloro Diphenyl Trichloro Ethane)

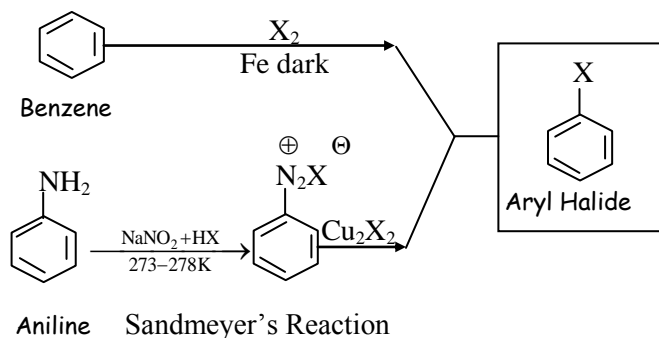
Chloral + 2 molecules of Chlorobenzene →



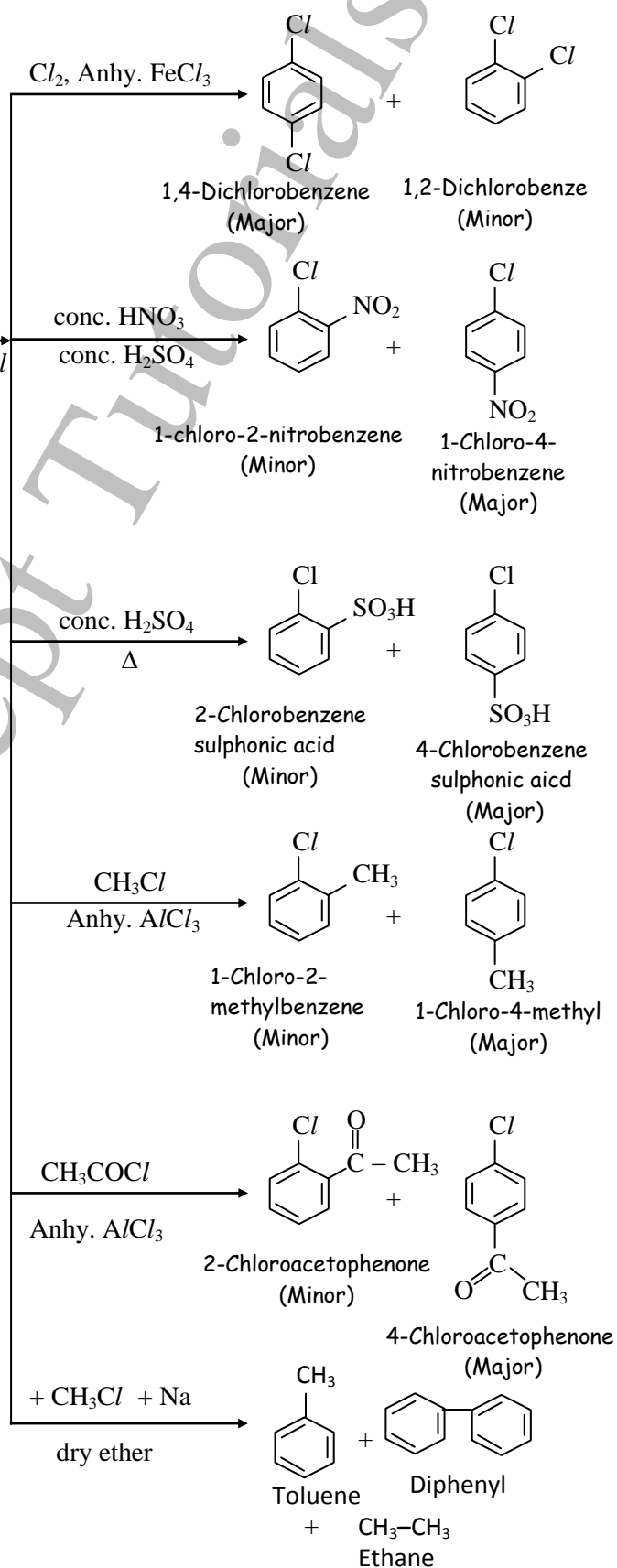
BRAIN MAPS**Preparation of alkyl halide (Haloalkanes)****Reaction of alkyl halide (Haloalkanes)**

* = best reagent in the category

Preparation of Haloarenes



Reaction of Haloarenes



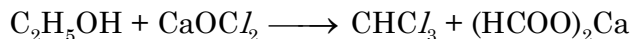
Wurtz Fittig Reaction

ADDITIONAL INFORMATION

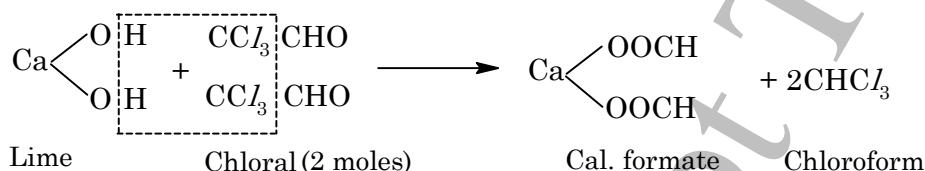
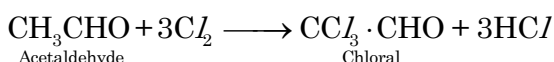
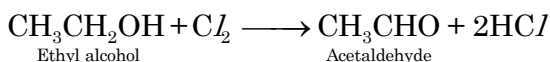
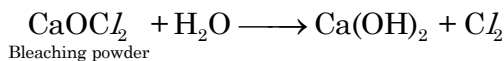
1. Chloroform, Trichloromethane, CHCl_3

Preparation :

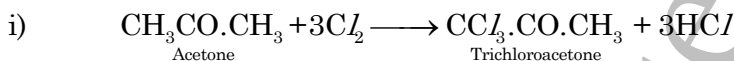
a) **From ethyl alcohol (or acetone) and bleaching powder.**



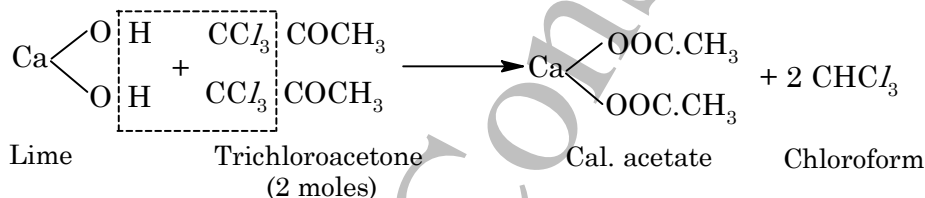
Mechanism :



Similarly, reactions taking place in case of acetone are as below:



ii)

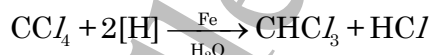


2. From methane (Industrial method): Chlorination of methane in presence of sunlight gives a mixture of different compounds

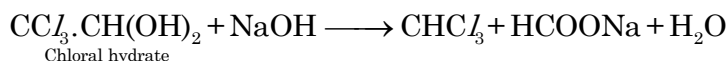
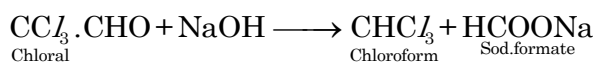


Chloroform is separated from other possible products by fractional distillation.

3. From carbon tetrachloride: (industrial method): Chloroform is produced by the partial reduction of CCl_4 with iron filings and water.



4. From chloral : Pure chloroform, **required for anaesthetic use is prepared by the action of aqueous sodium**

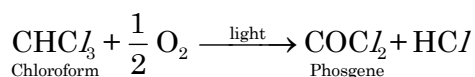


Physical Properties

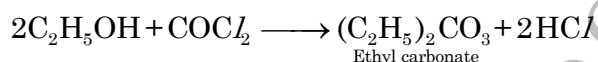
1. Chloroform is a heavy colourless liquid (b.p.61°C) with a characteristic sweet smell and sweet taste.
2. It is almost insoluble in water but soluble in alcohol and ether. It itself is a good solvent for oils, fats, resins, waxes, halogens, etc.
3. Inhalation of its vapours produces unconsciousness and hence it finds use as a general anaesthetic. However, owing to its bad effect on heart it has now been replaced by better anaesthetic like ether, ethylene and ethylene chloride.
4. Under ordinary conditions, it is not inflammable but its vapours when ignited burn with a green-edged flame.

Chemical Properties

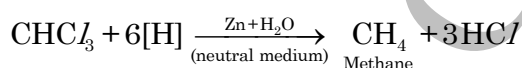
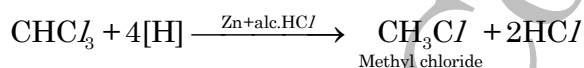
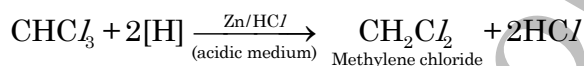
1. **Oxidation:** When exposed to air and sunlight, chloroform is slowly oxidised to carbonyl chloride (phosgene), a highly poisonous substance.



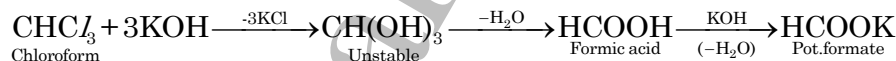
To avoid the oxidation of CHCl_3 to phosgene, chloroform (especially that meant for anesthetic purposes) is always stored in dark coloured bottles to cut off light. The bottles are filled to the neck and well stoppered to exclude air. A small amount of alcohol is also added to prevent the oxidation of chloroform and to convert phosgene (formed if any) to harmless ethyl carbonate.



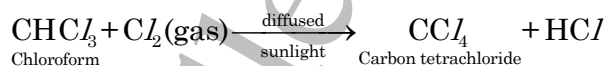
2. **Reduction:** Different products are formed under different conditions.



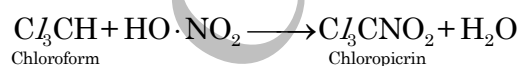
3. **Hydrolysis (action of aqueous KOH):**



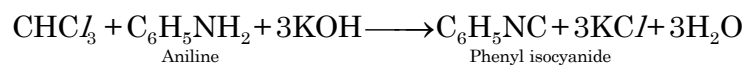
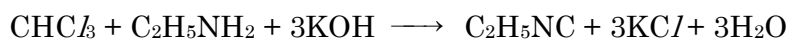
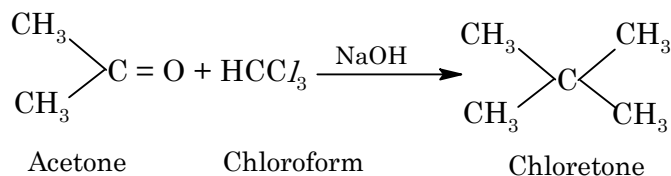
4. **Chlorination:**



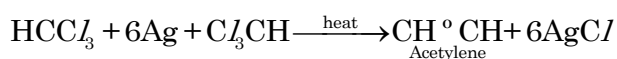
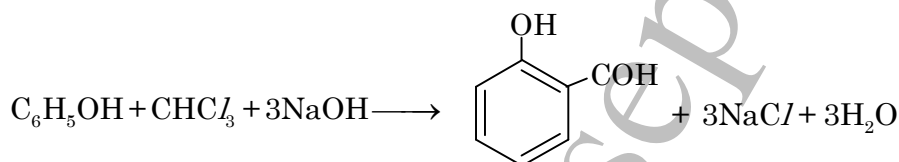
5. **Nitration (action of conc. HNO_3).**



Chloropicrin or **nitrochloroform** is a liquid and used as insecticide.

6. Carbylamine reaction (action of alcoholic potash and primary amine).**7. Condensation with ketones, e.g., acetone**

Chloretone, a colourless solid, is used as hypnotic.

8. Heating with silver powder (dehalogenation)**9. Reaction with phenol and alkali (Reimer-Tiemann reaction)**

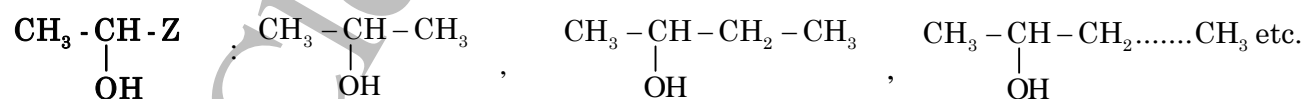
Chloroform is used :

- (i) as an anaesthetic
- (ii) as a solvent for fats, oils, waxes, rubbers, etc.
- (iii) in laboratory for testing primary amines
- (iv) in the preparation of chloropicrin (an insecticide) and chloretone (a hypnotic)
- (v) as preservative for anatomical specimens

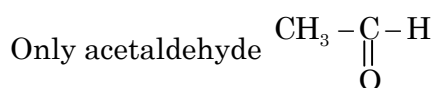
CHLOROFORM TEST :

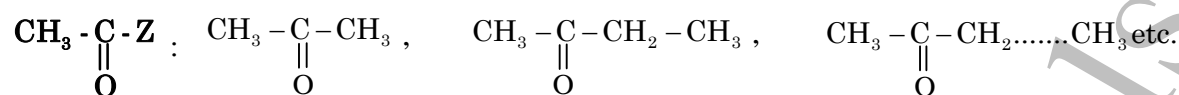
(+) ve haloform reaction: Reaction which gives haloform with alkali and X_2 is called as (+) ve haloform reaction.

Alcohols:

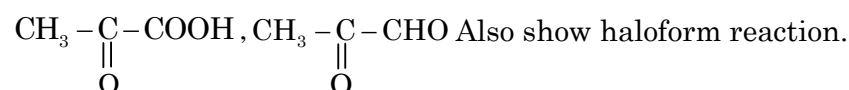
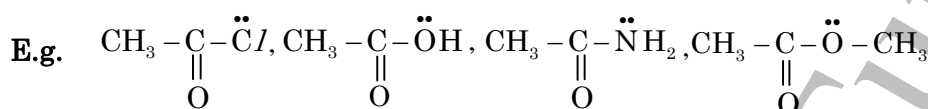


Aldehydes:



Ketones:

(All methyl ketones)

(-) ve haloform reaction: Reaction in which haloforms are not formed with X_2 and alkali.

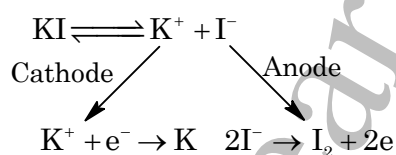
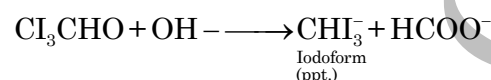
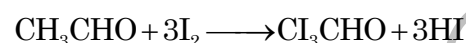
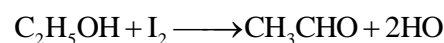
do not show haloform reaction.

Test of CHCl_3

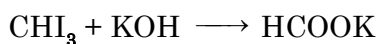
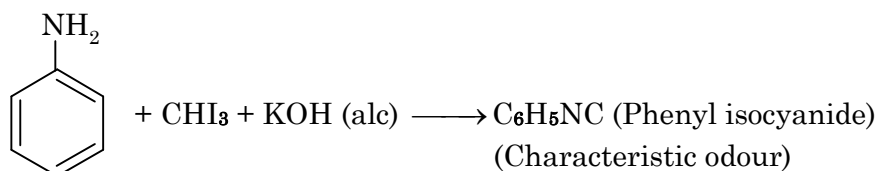
Reagent	Pure CHCl_3	Impure CHCl_3 ($\text{COCl}_2 + \text{HCl}$)
• Blue litmus	No Change	turn into red
• AgNO_3	No reaction	White ppt of AgCl
• Conc. H_2SO_4	No reaction	Yellow solution

iodoform**Preparation**

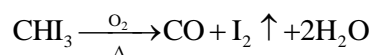
Iodoform resembles chloroform in methods of preparation

Laboratory Preparation :KOH is neutralised by CO_2 **Physical Properties**

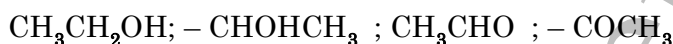
- (1) Yellow crystalline solid
- (2) Pigment characteristic odour
- (3) Insoluble in water

Hydrolysis**Reduction****Carbylamine Reaction**

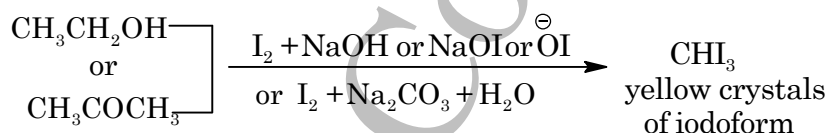
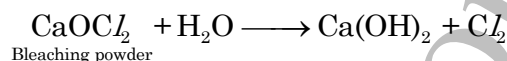
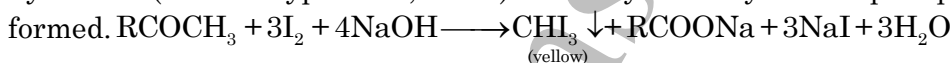
(This is a characteristic reaction of amines)

Heating Alone**Iodoform Test**

Formation of iodoform is commonly used as a test for detecting the presence of following compounds/groupings.



The test is carried out by warming the above type of compound with iodine and sodium hydroxide (sodium hypoiodite, NaOI) when a yellow crystalline precipitate of iodoform is formed.



CHI_3 give yellow ppt. Of AgI with AgNO_3 but CHCl_3 does not give AgCl ppt.

Reason: CHI_3 is thermally less stable than CHCl_3 .

Iodoform test can be used to distinguish the following pairs of compounds.

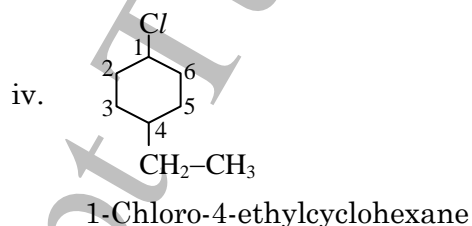
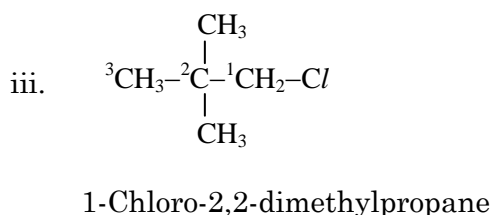
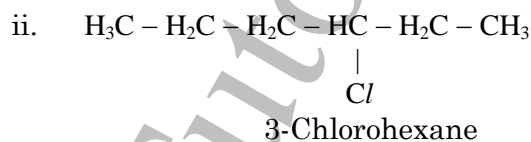
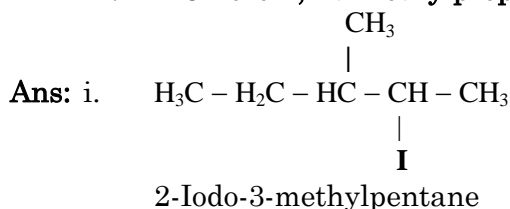
- i) $\text{CH}_3\text{CH}_2\text{OH}$ and CH_3OH
- ii) CH_3CHO and $\text{CH}_3\text{CH}_2\text{CHO}$
- iii) 2-Pentanol and 3-Pentanol
- iv) Acetophenone and benzophenone
- v) 2-Propanol and 1-Propanol

Intext Questions and Answers

1) GSB Unsolved Intext questions:

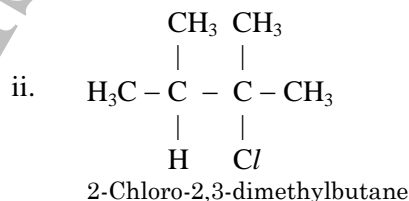
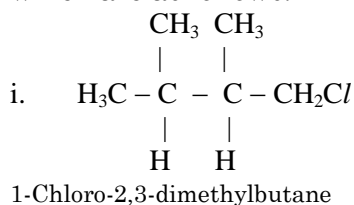
Q.1. Write the structures of following organic halogen compounds: (Page no. 376)

- i. 2-Iodo-3-methylpentane ii. 3-Chlorohexane
 iii. 1-Chloro-2,2-dimethylpropane iv. 1-Chloro-4-ethylcyclohexane



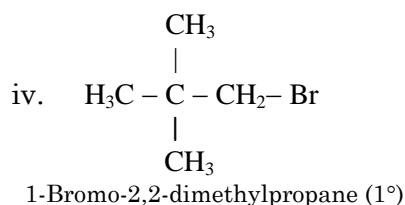
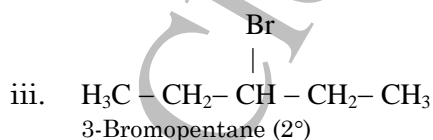
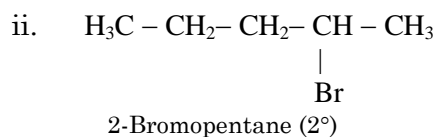
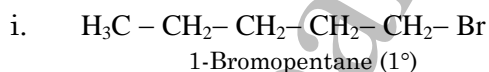
Q.2. Write the possible isomers of monochloro derivatives of 2,3-Dimethylbutane and write their IUPAC names. (Page no. 376)

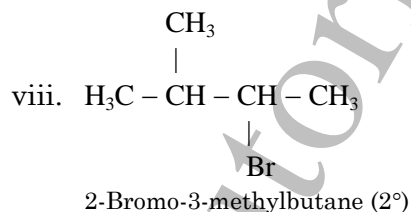
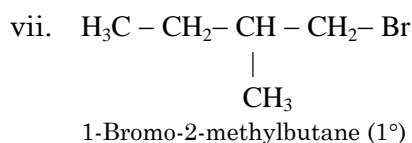
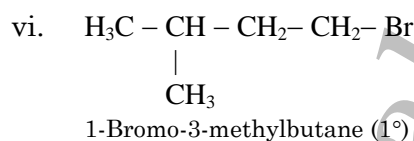
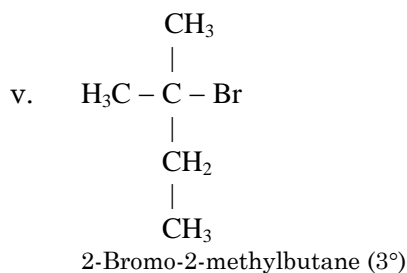
Ans: There are only two isomers possible for monochloro derivatives of 2,3-Dimethylbutane which are as follows:



Q.3. Write the structures and IUPAC names of all possible isomers of C₅H₁₁Br and classify them as primary (1°) / secondary (2°) / tertiary (3°). (Page no. 376)

Ans: Eight isomers of C₅H₁₁Br are:

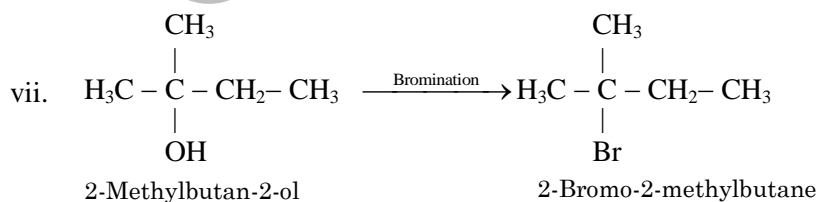
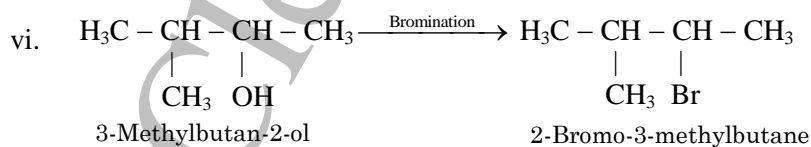
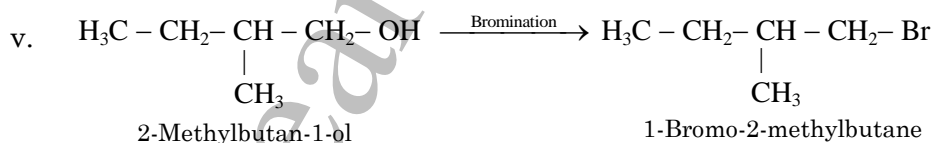
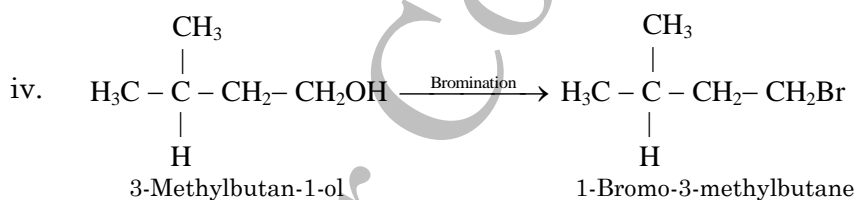
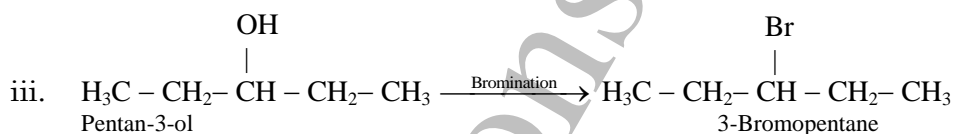
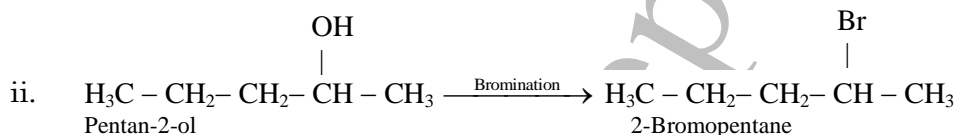
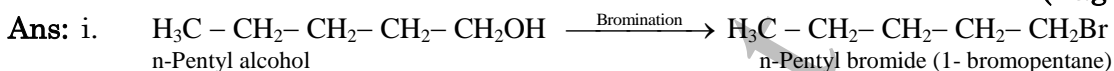


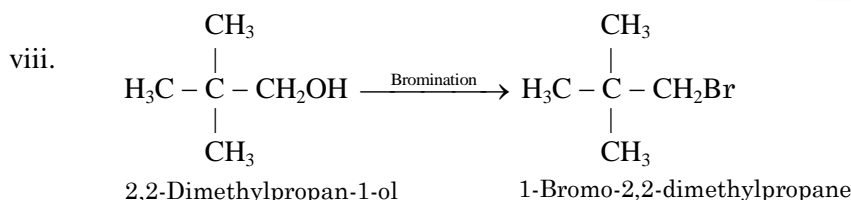


Conclusion: 1° C₅H₁₁Br = 4 compounds
3° C₅H₁₁Br = 3 compounds

2° C₅H₁₁Br = 3 compounds

Q.4. C₅H₁₁OH gives compound C₅H₁₁Br. Suggest all possible structures of alcohol and bromide.
(Page no. 382)

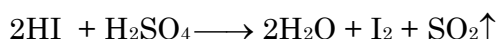
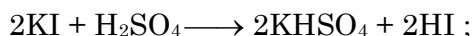




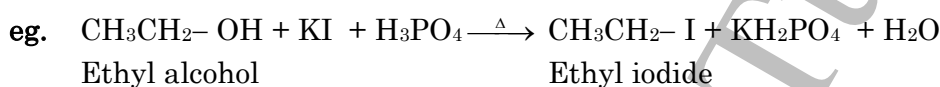
Q.5. Why is sulphuric acid not used during the reaction of alcohols with KI?

(Page no. 382)

Ans: H_2SO_4 is an oxidising agent. It oxidises HI produced during the reaction to I_2 .



As a result, it prevents the reaction between an alcohol and HI to form an alkyl iodide. Therefore, in order to overcome this difficulty, a non-oxidising acid such as H_3PO_4 is used instead of H_2SO_4 .



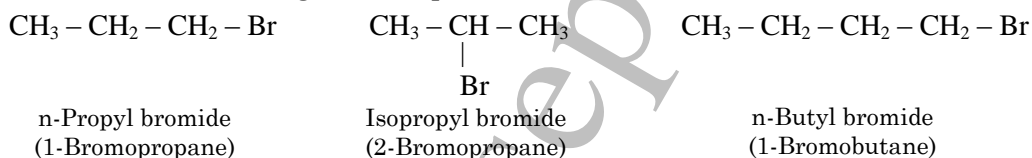
Q.6. Arrange each set of compounds in order of increasing boiling points:

i. 1-

Bromopropane, Isopropyl bromide, 1-Bromobutane.

(Page no. 383)

Ans: i. The structures of the given compounds can be written as follows:



- For the same halogen, boiling point increases as the size of the alkyl group increases.
- Therefore, the boiling point of 1-Bromobutane is higher than those of 1-Bromopropane and Isopropyl bromide.
- The boiling point decreases as the branching increases, therefore, the boiling point of 1-Bromopropane is higher than that of Isopropyl bromide.
- So, the boiling points of the three compounds increase in the order:
Isopropyl bromide < 1-Bromopropane < 1-Bromobutane.

Q.7. Assume that your both hands are equally strong and efficient, which of the following operations you will be able to do with same speed and efficiency?

(Page no. 391)

- Cutting an apple with a knife.
- Opening a bottle with threaded cap.
- Cutting a piece of wood with a saw.
- Cutting a piece of paper with scissor.
- Turning on a water tap.
- Lifting a ball point pen.

Ans: Turning on a water tap and lifting a ball point pen can be done with both hands with the same speed and efficiency.

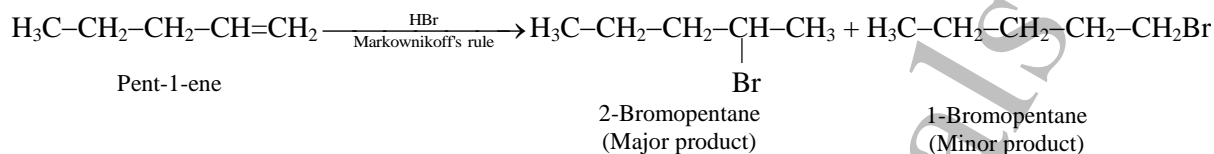
Q.8. Complete the following reactions and explain optical activity of the products formed.

Reaction of

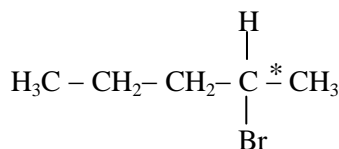
- pent-1-ene with HBr
- pent-2-ene with HBr.

(Page no. 391)

Ans: i. Pent-1-ene reacts with HBr in the following manner,

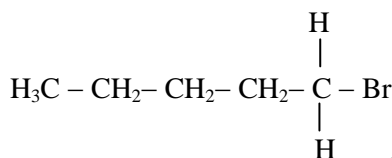


The products formed by the reaction of pent-1-ene with HBr are 2-Bromopentane and 1-Bromopentane. As 2-Bromopentane consists of one asymmetric carbon atom, it is optically active.



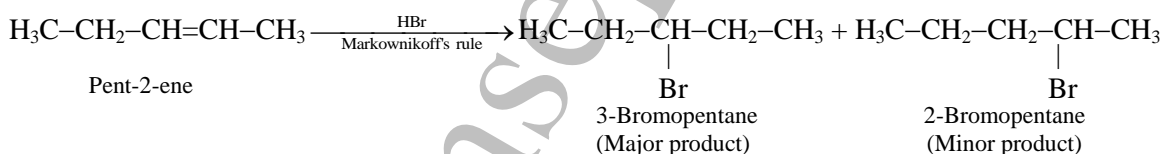
2-Bromopentane (optically active)

However, 1-Bromopentane lack asymmetric carbon atom and therefore, it is optically inactive.

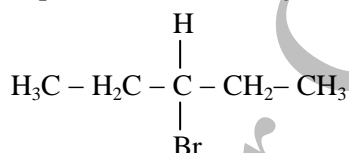


1-Bromopentane (optically inactive)

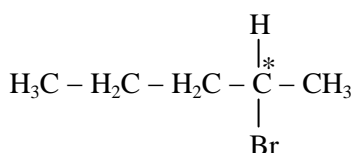
ii. Pent-2-ene reacts with HBr in the following manner,



The products formed by the reaction of pent-2-ene with HBr are 3-Bromopentane and 2-Bromopentane. 3-Bromopentane is optically inactive compound due to the absence of asymmetric carbon atom while 2-Bromopentane is optically active due to the presence of one asymmetric carbon atom.



3-Bromopentane
(optically inactive)

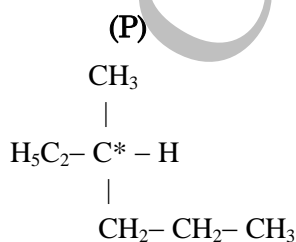


2-Bromopentane
(optically active due to the presence of one asymmetric carbon atom)

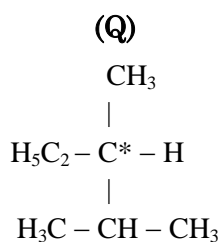
Q.9. Compounds P and Q are lowest molecular weight alkanes, which are optically active. Draw their structures and write their IUPAC names.

(Page no. 391)

Ans:

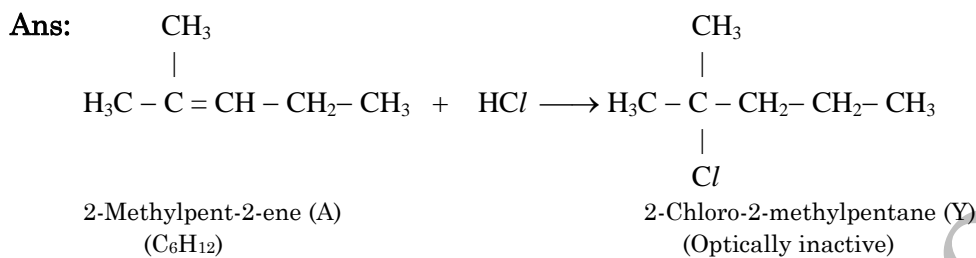


3-Methylhexane



2,3-Dimethylpentane

Q.10. C_6H_{12} (A) on treatment with HCl produced only one compound Y, which is optically inactive. What is the structure of A? (Page no. 391)



Q.11. List the substituents in each of the following sets in order of priority, from highest to lowest:

- i. $-\text{CH}_2-\text{Br}$, $-\text{SH}$, $-\text{CH}_3$ and $-\text{CH}_2-\text{OH}$
 ii. $-\text{CH}=\text{CH}_2$, $-\text{CH}(\text{CH}_3)_2$, $-\text{C}\equiv\text{N}$ and $-\text{OCH}_3$

(Page no. 392)

- Ans: i. $-\text{SH} > -\text{CH}_2-\text{Br} > -\text{CH}_2-\text{OH} > -\text{CH}_3$
 ii. $-\text{OCH}_3 > -\text{C}\equiv\text{N} > -\text{CH}=\text{CH}_2 > -\text{CH}(\text{CH}_3)_2$

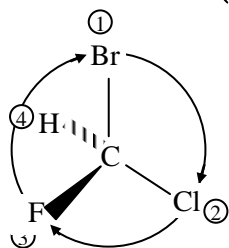
Q.12. Write the enantiomeric forms of :

- i. Bromochlorofluoromethane ii. Butan-2-ol
 iii. glyceraldehyde iv. lactic acid

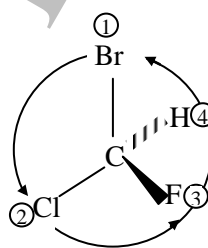
Assign each enantiomer (R) or (S) designation.

(Page no. 393)

Ans: i.



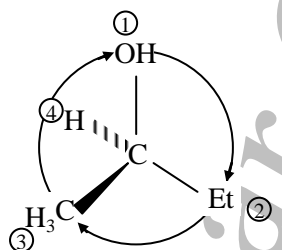
R-configuration



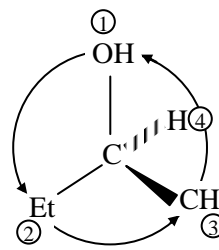
S-configuration

Bromochlorofluoromethane

ii.



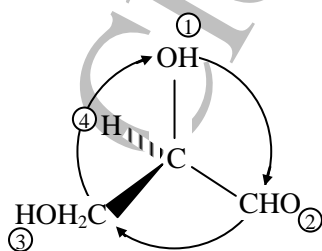
R-configuration



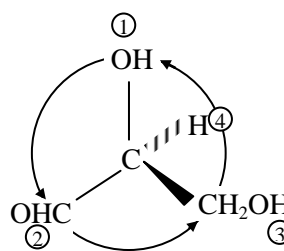
S-configuration

Butan-2-ol

iii.



R-configuration



S-configuration

Glyceraldehyde

iv.

R – configuration

Lactic acid

S – configuration

Q.13. Predict the order of reactivity by S_N1 or S_N2 reaction. (Page no. 399)

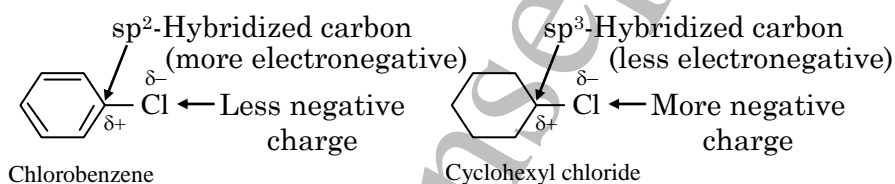
$C_6H_5CH(CH_3)Cl$, $C_6H_5C(CH_3)(C_6H_5)Cl$, $C_6H_5CH_2Cl$, $C_6H_5CH(C_6H_5)Cl$

Ans: $C_6H_5C(CH_3)(C_6H_5)Cl > C_6H_5CH(C_6H_5)Cl > C_6H_5CH(CH_3)Cl > C_6H_5CH_2Cl$ (S_N1)

$C_6H_5C(CH_3)(C_6H_5)Cl < C_6H_5CH(C_6H_5)Cl < C_6H_5CH(CH_3)Cl < C_6H_5CH_2Cl$ (S_N2)

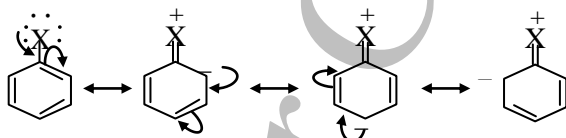
Q.14. The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride. Explain. (Page no. 383)

- Ans:**
- In both the compounds, C–Cl bond is polar due to high electronegativity of chlorine.
 - In case of chlorobenzene, carbon to which chlorine is attached is sp^2 hybridized and is more electronegative than carbon in cyclohexyl chloride which is sp^3 hybridized. So the net dipole moment is lower in chlorobenzene.



Q.15. Explain, why aryl halides are less reactive than alkyl halides. (Page no. 404)

- Ans:**
- In haloarenes, the electron pairs on halogen atom are in conjugation with π -electrons of the ring. So, the bond cleavage in haloarenes is difficult than haloalkanes.



- Due to the resonance, the C–X bond in aryl halides possesses double bond character.
- The sp^2 hybridized carbon has greater s-character and is more electronegative due to which it holds the electron pair of C–X bond more tightly.



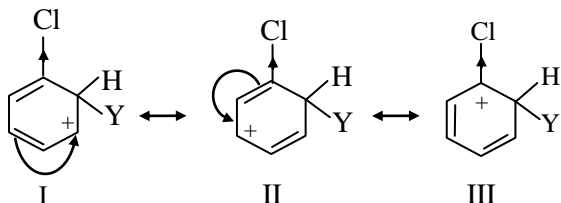
- In case of haloarenes, the phenyl cation produced due to self ionization will not be stabilized by resonance, which rules out the possibility of S_N1 mechanism.
- Due to repulsion, the electron rich nucleophile will not approach electron rich arenes which rules out S_N2 mechanism. So, aryl halides are less reactive than alkyl halides.

Q.16. Draw the resonating structures of the carbocations formed by electrophilic

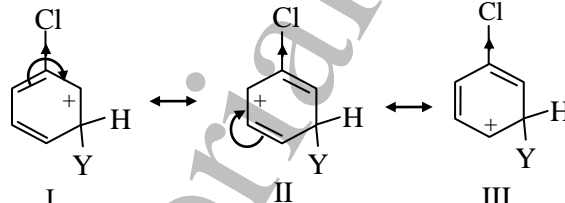
substitution, by the attack of an electrophile (Y) on Chlorobenzene, at ortho, meta and para positions. (Page no. 404)

Ans: The carbocation formed by the attack of electrophile (Y) on Chlorobenzene at ortho, meta, para positions are as shown below:

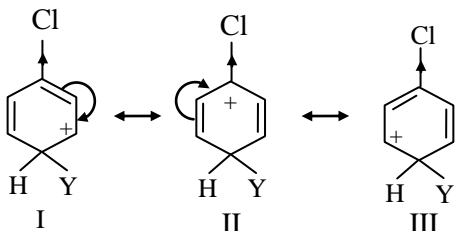
i. **Ortho attack:**



ii. **Meta attack:**



iii. **Para attack:**



Q.17. Explain, bromobenzene is o, p directing for substitution reactions.

(Page no. 404)

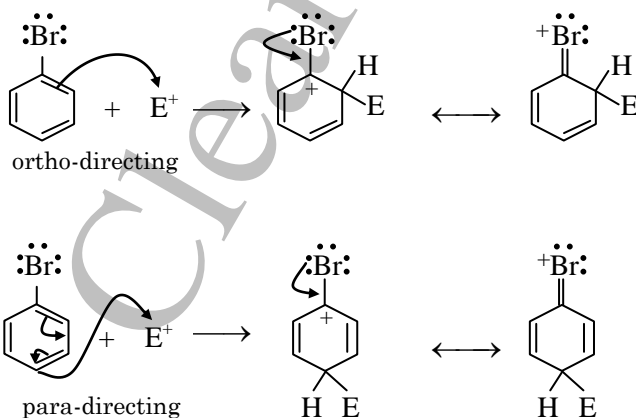
- Ans:**
- Bromine withdraws electron through inductive effect (-I) and releases electron through resonance (+M).
 - Bromine destabilizes the intermediate carbocation formed during the electrophilic substitution through inductive effect. (-I effect)

- I - Effect of Br destabilizes the intermediate carbocation



- Through resonance(+M effect), halogen tends to stabilise the carbocation and the effect is more pronounced at ortho- and para- position.

+R - Effect of Br stabilizes the intermediate carbocation



- The inductive effect is stronger than resonance and causes net electron withdrawal and this causes net deactivation.
- The resonance effect tends to oppose the inductive effect for the attack at ortho- and

para-positions and hence, makes the deactivation less for ortho- and para- attack.

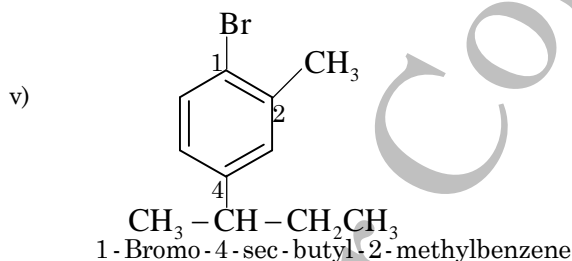
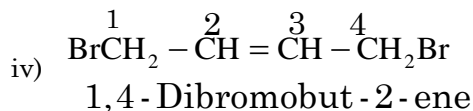
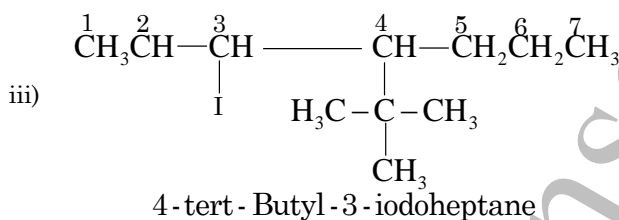
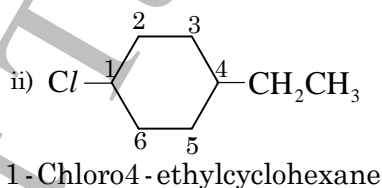
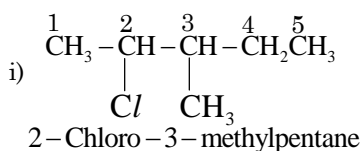
- vi. Reactivity is thus controlled by the **stronger inductive effect** and **orientation is controlled by weaker resonance effect**. So bromobenzene is o, p directing for substitution reactions.

2) NCERT Unsolved Intext questions:

Q. 10.1. Write the structures of the following compounds :

- i) 2-Chloro-3-methylpentane ii) 1-Chloro-4-ethylcyclohexane
iii) 4-tert-Butyl-3-iodoheptane iv) 1, 4-Dibromobut-2-ene
v) 1-Bromo-4-sec-butyl-2-methylbenzene.

(Page no. 285)



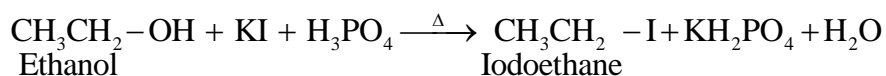
Q.10.2. Why is sulphuric acid not used during the reaction of alcohols with KI ?

(Page no. 289)

Ans: H_2SO_4 is an oxidising agent. It oxidises HI produced during the reaction to I_2 and



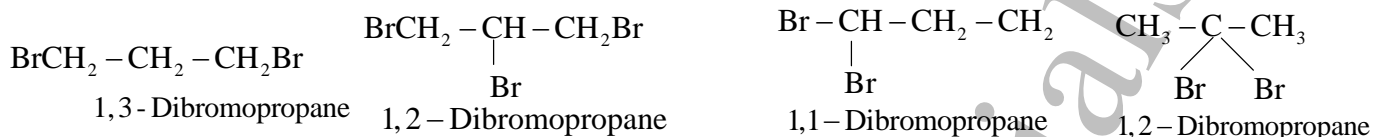
thus prevents the reaction between an alcohol and HI to form an alkyl iodide. To overcome this difficulty, a non-oxidising acid such as H_3PO_4 is used instead of H_2SO_4 .



Q. 10.3 Write structures of different dihalogen derivatives of propane.

Ans: Four isomeric dihalogen derivatives of propane are formed for each halogen.

For example



Similarly, we can write four isomeric dihalogen derivatives for other halogens.

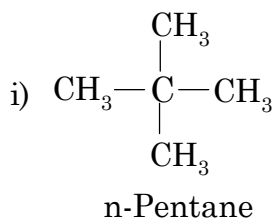
Q. 10.4. Among the isomeric alkenes of molecular formula C_5H_{10} , identify the one that on photochemical chlorination yields.

i) A single monochloride

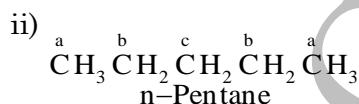
ii) Three isomeric monochlorides

iii) Four isomeric monochlorides

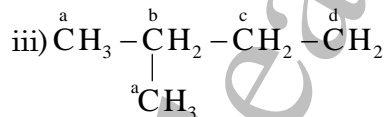
Ans: All the H atoms are equivalent. Therefore, replacement of any one of them will give the same product.



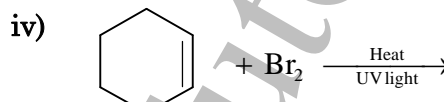
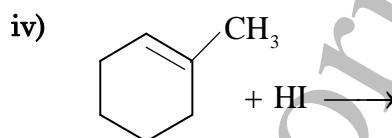
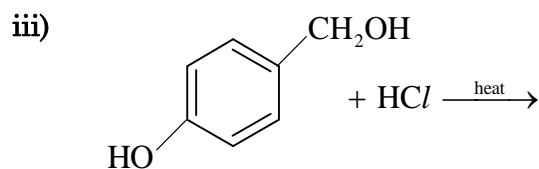
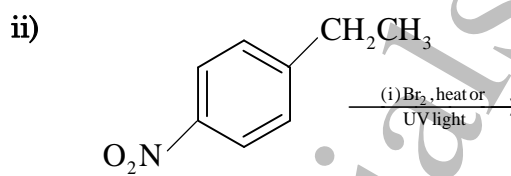
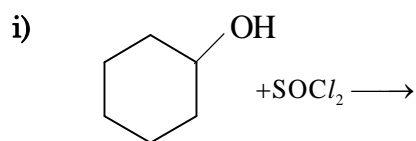
There are three sets of equivalent hydrogen's designated as a, b and c. The replacement of any one of the equivalent hydrogen's of each set will give the same product. Therefore, three isomeric monochlorides are possible.



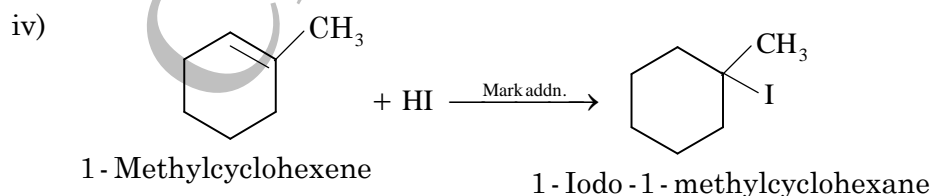
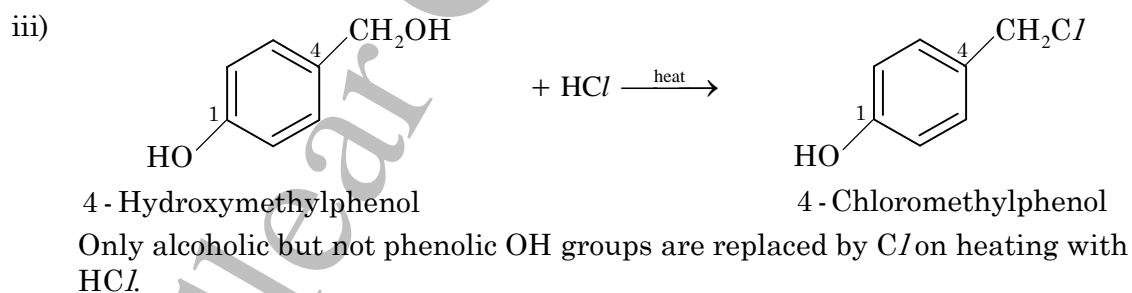
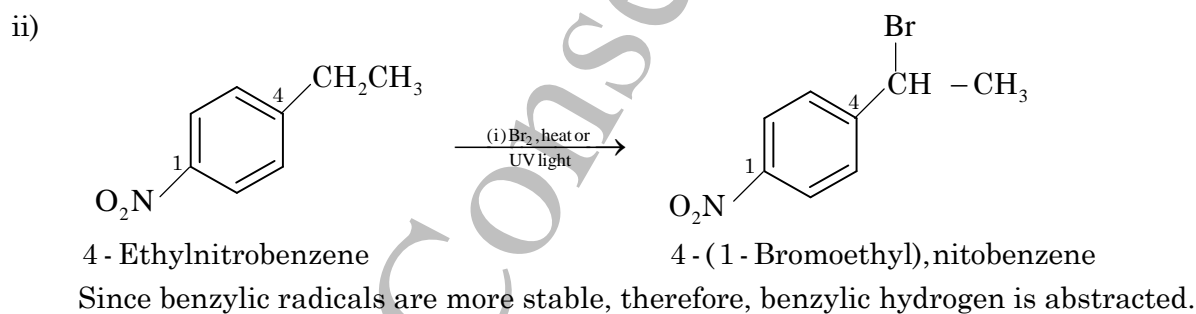
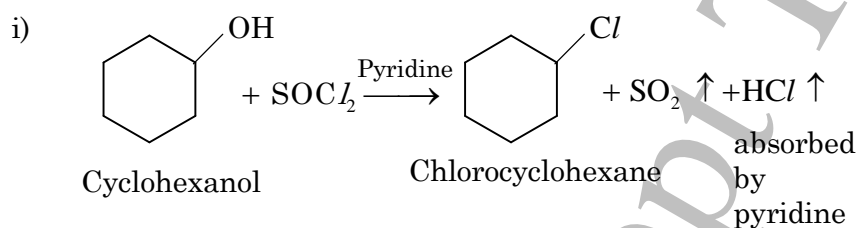
There are four types of equivalent hydrogens designated as a, b, c and d. Therefore, four isomeric monochlorides are possible.

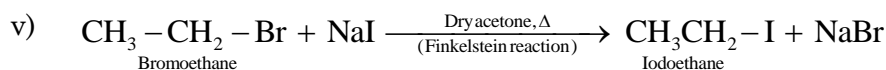


Q. 10.5. Draw the structures of major monohalo products in each of the following reactions. (Page no. 289)

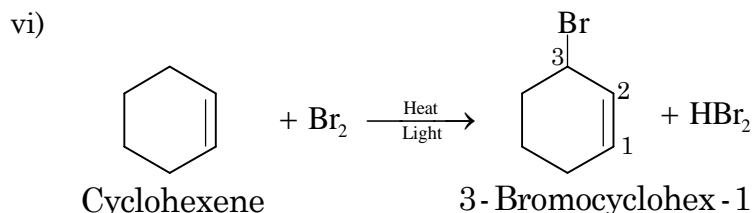


Ans:





Iodide ion is a stronger nucleophile and hence it displaces bromide ion. Further since NaBr is insoluble while NaI is soluble in dry acetone, therefore, the equilibrium shifts in the forward direction.



In presence of heat and light, allylic bromination occurs to form 3-bromocyclohex-1-ene.

Q. 10.6. Arrange each set of compounds in order of increasing boiling points.

(i) Bromomethane, bromoform, chloromethane, dibromomethane.

(ii) 1-Chloropropane, isopropyl chloride, 1-chlorobutane.

(Page no. 291)

Ans:

- i) For the same alkyl group, boiling point increases with the size of the halogen atom. Therefore, boiling point of bromomethane is higher than that of chloromethane. Further, the boiling points increase as the number of halogen atoms increases. Therefore, the boiling point of bromoform with three Br atoms is the highest, followed by dibromomethane with two Br atoms while bromomethane with one Br atom is the lowest. Combining all the arguments presented above, the boiling points of the four compounds discussed above increase in the order:
chloromethane < bromomethane < dibromomethane < bromoform.
- ii) For the same halogen, boiling point increases as the size of the alkyl group increases. Therefore, the boiling point of 1-chlorobutane is higher than those of 1-chloropropane and isopropyl chloride. Further, the boiling point decreases as the branching increases, therefore, the boiling point of 1-chloropropane is higher than that of isopropyl chloride. Combining these two arguments, the boiling points of the three compounds discussed above increase in the order:
Isopropyl chloride < 1- chloropropane < 1- chlorobutane.

Q.10.7. Which alkyl halide from the following pairs would you expect to react more rapidly by S_N2 mechanism? Explain your answer. (Page no. 307)

- i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ or $\text{CH}_3\text{CH}_2-\underset{\text{Br}}{\text{CH}}-\text{CH}_3$ ii) $\text{CH}_3\text{CH}_2-\underset{\text{Br}}{\text{CH}}-\text{CH}_3$ or $\text{H}_3\text{C}-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{Br}$
- iii) $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2\text{CH}_2\text{Br}$ or $\text{CH}_3\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2\text{Br}$

Ans:

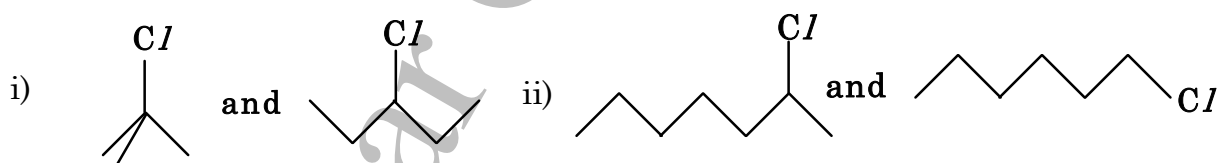
- i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ is a 1° alkyl halide while $\text{CH}_3\text{CH}_2-\text{CHBr}-\text{CH}_3$ is a 2° alkyl halide. Since there will be some steric hindrance in 2° alkyl halides than in 1° alkyl halides, therefore, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ will react faster than $\text{CH}_3\text{CH}_2-\text{CHBr}-\text{CH}_3$ in S_N2 reaction.
- ii) $\text{CH}_3\text{CH}_2-\text{CHBr}-\text{CH}_3$ is a 2° alkyl halide while $(\text{CH}_3)_3\text{C}-\text{Br}$ is 3° alkyl halide. Since due to lesser steric hindrance, 2° alkyl halides react faster than 3° alkyl halides, therefore, $\text{CH}_3\text{CH}_2-\text{CHBr}-\text{CH}_3$ will react faster than $(\text{CH}_3)_3\text{CBr}$ in S_N2 reaction.



Both I and II are 2° alkyl halides. But in alkyl halide (II), the CH_3 group at C_2 is closer to the Br atom while in alkyl halide (I), the CH_3 group at C_3 is little away from the Br atom. As a result, alkyl halide (I) will suffer greater steric hindrance than alkyl halide (II).

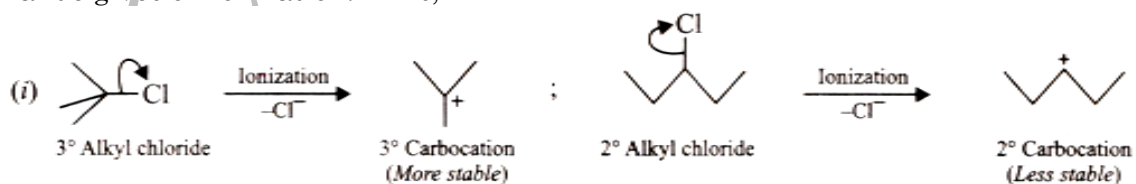
Therefore, $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$ will react faster than $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Br}$ in S_N2 reaction.


Q.10.8. In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction? (Page no. 307)



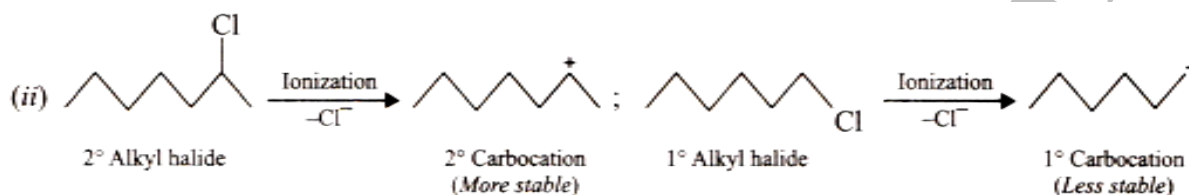
Ans:


The reactivity in S_N1 reaction is governed by stability of the intermediate carbocation which an alkyl halide gives on ionization. Thus,



Since 3° carbocations are more stable than 2° carbocations, therefore  Cl will react

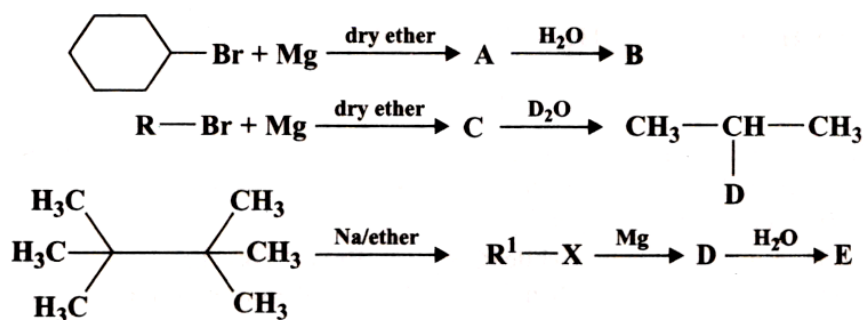
faster than  in S_N1 reaction.



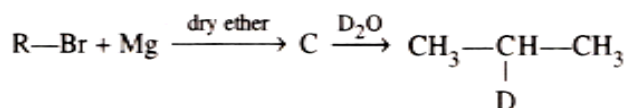
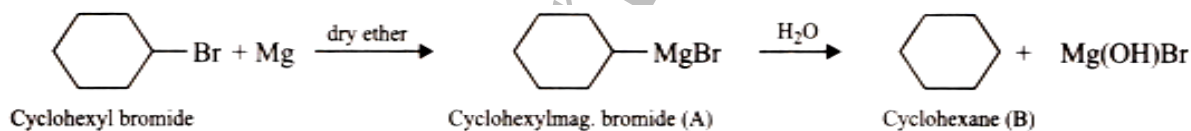
Since 2° carbocations are more stable than 1° carbocations, therefore  will react

faster than  Cl in S_N2 reaction.

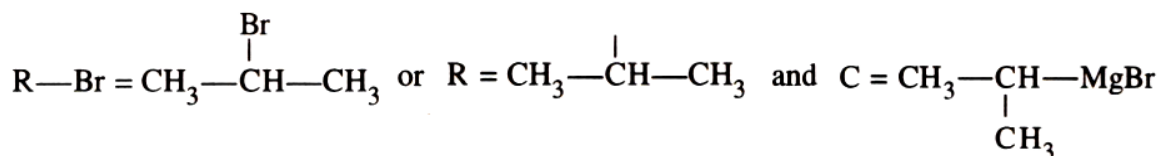
Q.10.9. Identify A, B, C, D, E, R and R in the following: (Page no. 307)



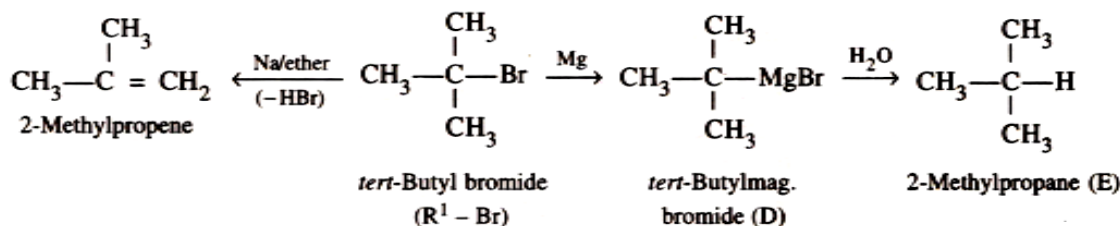
Ans:



Since D gets attached to the same carbon atom on which MgX was present, therefore



The third part of the question is wrong because tert-alkyl halides do not undergo Wurtz reaction but undergo dehydrohalogenation to give alkenes. Thus, R₁ = (CH₃)₃C— and hence D and E are

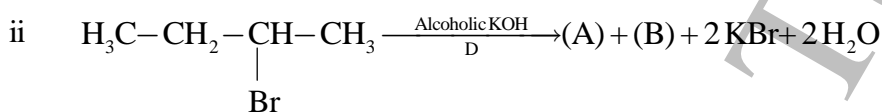
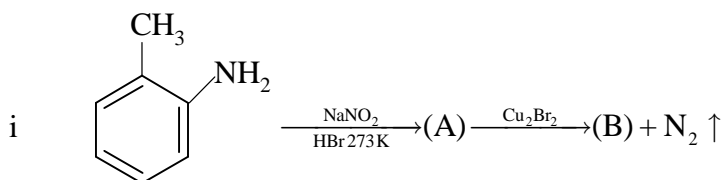


HSC Board Exam Questions

(Syllabus changed from 2013 onwards)

- 1] What are the compounds represented by formula $C_2H_4Cl_2$? [March 13 old course]
- 2] Write the structures of: [Oct. 14]
i) 3-Chloro-3-ethylhex-1-ene ii) 1-Iodo-2,3-dimethylbutane
- 3] State and explain Markownikoff's rule with suitable example. [Oct. 14]
- 4] How is propene converted into 1-bromopropane and 2-bromopropane? [March 16]
- 5] Write the balanced chemical equation for the action of hydrogen bromide on styrene in the presence of a peroxide. [March 13]
- 6] What is the action of the following reagent on ethyl bromide? Sodium ethoxide [March 13 old course]
- 7] Write balanced chemical equation for the action of methyl bromide on silver propanoate. [March 13]
- 8] What is Grignard reagent? How is it prepared? [March 13 old course, March 19]
- 9] Identify 'A' and 'B' in the following reaction : [Oct. 15]
 $CH_3 - CH = CH_2 \xrightarrow{HBr} 'A' \xrightarrow{alc.KOH} 'B'$
- 10] Define optical activity. [July 17]
- 11] Explain the term: optical activity. [March 16]
- 12] Define racemic mixture. [March 17]
- 13] Explain the optical activity of lactic acid. [March 14, July 17]
- 14] Explain the mechanism of alkaline hydrolysis of bromomethane with energy profile diagram. [March 13 old course]
- 15] Discuss the mechanism of alkaline hydrolysis of bromomethane. [Oct. 15]
- 16] Draw a neat, labelled energy profile diagram for S_N^1 reaction mechanism. [Oct 13]
- 17] Explain the mechanism of alkaline hydrolysis of tert-butyl bromide with energy profile diagram. [March 17, 18]

- 18] Distinguish between S_N^1 and S_N^2 mechanisms . [March 14]
- 19] Write the structure of 1,3,5-Tribromobenzene. [Oct. 14]
- 20] Write a note on Sandmeyer's reaction [July 16]
- 21] Identify 'A' and 'B' and rewrite the reactions' [July 16]



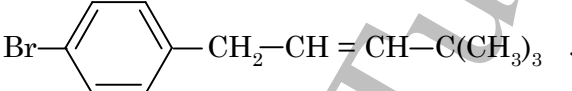
- 22] Why does p-nitrochlorobenzene undergo displacement reactions readily with attack of nucleophilic OH^- ion. [March 13]
- 23] Write a note on Friedel Craft's acylation. [March 15]
- 24] How is chlorobenzene prepared from aniline? How is chlorobenzene converted into diphenyl? [March 16]
- 25] Draw structure of DDT. Write its environmental effects. [Mach 15]
- 26] i) Complete and rewrite the balanced chemical equations [Mach 18]
- a) Chlorobenzene $\xrightarrow[473\text{K, pressure}]{\text{NaCN} + \text{CuCN}} ?$
- 27] What is the action of the following on ethyl bromide [Mach 19]
- (i) alcoholic solution of potassium hydroxide.
- (ii) moist silver oxide
- (iii) silver acetate?
- 28] Define Enantiomers. [Mach 19]

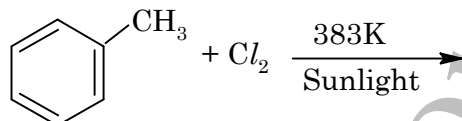
Theory Question Bank Given By Board

Note:

- 1) Practice of these questions will help in developing the chapter.
- 2) Every 1 mark questions means to write two points
- 3) Every 2 marks questions means to write four points. (So on ...)
- 4) Following questions will help for college theory exam.
- 5) Write all answers in separate Long book.

1] **Very Short Answer Questions (VSA) (1 Mark With Difficulty Level)**

- 1.1) Write IUPAC name of 
- 1.2) Write Structure of tert-alkyl halide having molecular formula $C_5H_{11}Br$.
- 1.3) Give balanced chemical equation for the action of antimony trifluoride on 2, 2 -Dichloropropane.
- 1.4) What is IUPAC name of an alcohol used in the preparation of 2-Chloro-2, 4 -dimethylhexane.
- 1.5) Draw the structure of the major monohaloproduct obtained in the following reaction.



- 1.6) How is Bromoethane converted into Ethylcarbylamine?
- 1.7) Write IUPAC name of product expected from reaction of Sodium methoxide with Isobutylbromide.
- 1.8) Monochloroderivative (A) when dissolved in ether and treated with sodium metal gives single hydrocarbon product 2,2,5,5-Tetramethylhexane, what is the formula of compound A?
- 1.9) Which isomer of C_4H_9Cl will have the lowest boiling point?
- 1.10) Which reagent is used to introduce nitro group in haloarenes?
- 1.11) Give balanced chemical equation for the reaction of chlorobenzene with acetyl chloride.
- 1.12) Arrange the following groups in descending order of priority in assigning R, S configuration. $-NH_2$, $-SO_3H$, $-OCH_3$, $-COOH$ and $-Cl$
- 1.13) Compound A (C_4H_8) on treatment with HBr gives compound B which is optically inactive. What is structure of A?
- 1.14) Which polyhalide is used as dry cleaning agent and as a pesticide to kill insects in stored grains?

-
- 1.15) Write structural formula of DDT.
- 1.16) Why is sulphuric acid not used in reaction of alcohols with potassium iodide?
- 1.17) Alkyl fluorides are not prepared by halogenation of alkane. Give reason.
- 1.18) Write the name of reaction of alkyl chlorides or bromides with metallic fluorides, to form Alkyl Fluorides.

2]

Very Short Answer Questions - Section A

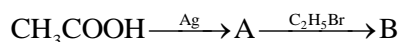
(which can be combined with Sections B / C / D)

- 2.1) What are halogen derivatives of alkanes?
- 2.2) What are alkyl halides?
- 2.3) Write IUPAC name of tert-butyl bromide.
- 2.4) Draw the structure of 1,2,3-Trichloropropane.
- 2.5) How is chloroethane prepared from ethane?
- 2.6) Write a chemical reaction for action of HBr on isopropyl alcohol
- 2.7) How is ethyl chloride prepared from alcohol using thionyl chloride?
- 2.8) What is the action of moist silver oxide on Bromoethane?
- 2.9) Write the name of product obtained by action of alcoholic KCN on ethyl bromide.
- 2.10) Write a chemical equation for action of alcoholic silver propionate on ethyl bromide.
- 2.11) How is ethene prepared from Bromoethane?
- 2.12) What is Grignard's reagent?
- 2.13) What is optical activity?
- 2.14) Define Asymmetric carbon atom.
- 2.15) What is dextro form?
- 2.16) What is laevo form?
- 2.17) What is Racemic form?
- 2.18) Write uses of iodoform.
- 2.19) Write IUPAC name of m-dibromobenzene.

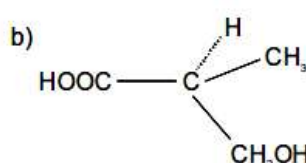
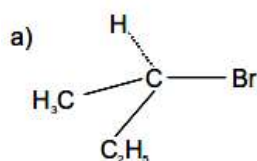
3)

Section B - Questions of 2 Marks SAI

- 3.1) How are following compounds obtained from alcohols using PCl_3 ?
- a) 2-Chloropropane b) 2-Chloro -2-methylpropane
- 3.2) Describe the action of excess of ammonia on
- a) Isopropyl bromide b) Isobutyl chloride
- 3.3) Identify A and B in the following.



- 3.4) How is 2-Chloropropane converted into 1-Bromopropane?
- 3.5) Explain Ammonolysis.
- 3.6) Explain dehydrohalogenation reaction of 2-Bromobutane.
- 3.7) What is Grignard's reagent? How is it prepared?
- 3.8) State and explain Markownikoff's Rule.
- 3.9) Predict the expected product and write balanced chemical equation for a substitution reaction of Isobutyl chloride with sodium ethoxide.
- 3.10) Define optical activity. Draw the structures of optical isomers of lactic acid.
- 3.11) Assign R or S designation to each of the following.



- 3.12) Write the reaction mechanism of reaction of o-nitrochlorobenzene with alkali.
- 3.13) Explain Friedel Crafts Alkylation reaction.
- 3.14) Explain Wurtz Fittig reaction with suitable example.
- 3.15) Write a note on Sandmeyer's reaction.
- 3.16) How is Ethanol converted into Butane?
- 3.17) How is Ethene converted into ethyl magnesium bromide?
- 3.18) How is propene converted into Butanenitrile?
- 3.19) Write uses of Freons.
- 3.20) Draw structural formula and write the IUPAC name of DDT.
- 3.21) Draw the resonating structures of chlorobenzene.

4)

Section C - Questions of 3 Marks SAI

- 4.1) Identify A, B and C in the following
- $$\text{Ethane} \xrightarrow[\text{AlBr}_3]{\text{Br}_2} \text{A} \xrightarrow[\Delta]{\text{alco. KOH}} \text{B} \xrightarrow{\text{HCl}} \text{C}$$
- 4.2) How are following compounds prepared from benzene diazonium chloride
- a) Chlorobenzene b) Bromobenzene c) Iodobenzene ?
- 4.3) How is chlorobenzene converted into
- a) Phenol b) Cyanobenzene c) Aniline ?
- 4.4) Give the mechanism of alkaline hydrolysis of Bromomethane.
- 4.5) Write the mechanism of alkaline hydrolysis of an alkyl halide which involves formation of carbocation as an intermediate.
- 4.6) Differentiate between S_N1 and S_N2 mechanism.

-
- 4.7) Define the following terms
a) Dextro form b) Laevo form c) Racemic form
- 4.8) Write balanced chemical equations for the action of following reagents on 2-Chlorobutane.
a) Aqueous potassium hydroxide
b) Sodium methoxide
c) Silver propionate
- 4.9) How is Iodoethane prepared from : a) Ethyl bromide b) Ethanol c) Ethene ?
- 4.10) How is Chloromethane converted into Ethyl magnesium bromide?
- 4.11) Explain nature of C–X bond in haloarenes.
- 4.12) The dipole moment of chlorobenzene is lower than cyclohexyl chloride. Explain.
- 4.13) Give balanced chemical equations for the following.
a) Action of AgF on Chloromethane,
b) Action of CoF₂ on Bromoethane,
c) Action of Hg₂F₂ on 1-Chloropropane.
- 4.14) Give reason : Haloarenes are less reactive towards the nucleophilic substitution reactions.
- 4.15) Write uses and environmental effect of chloroform.
- 4.16) Aryl halides undergo electrophilic substitution reaction slowly. Give reason.
- 4.17) Write structures and IUPAC names of all possible isomers of C₅H₁₁Br which are secondary alkyl halides.
- 4.18) Write enantiomeric forms of
a) Bromochlorofluoromethane b) Glyceraldehyde c) Butan-2-ol
- 4.19) Write uses and environmental effects of freons.