

8. HALOALKANES (ALKYL HALIDES)- CONTENTS

<https://subarnam.com.ng/>

Learning outcomes

After completing the chapter, the students should be able to:

1. Describe the nomenclature, isomerism, and classification of monohaloalkanes.
2. Explain the preparation of monohaloalkanes from alkanes, alkenes, and alcohols.
3. State the physical properties of haloalkanes.
4. Describe the chemical properties of haloalkanes: substitution reactions, SN^1 and SN^2 reactions (basic concept only).
5. Explain the formation of alcohols, nitriles, amines, ethers, thioethers, carbylamines, nitrites, and nitroalkanes using haloalkanes
6. Describe elimination reactions (dehydrohalogenation and Saytzeff's rule), reduction reactions, and the Wurtz reaction.
7. Show the preparation of trichloromethane from ethanol and propanone.
8. Explain the chemical properties of trichloromethane: oxidation, reduction, action on silver powder, conc. nitric acid, propanone, and aq. alkali

Introduction

Did you know that some of the most useful compounds in medicine, agriculture, and industry come from a simple idea: replacing hydrogen atoms in an alkane with halogen atoms? These compounds are called **haloalkanes** (also known as alkyl halides). They are important in many pharmaceuticals, refrigerants, solvents, and other industrial chemicals 🌿 Many pesticides contain haloalkanes. 🔍 Teflon (polytetrafluoroethylene, PTFE) is used in non-stick cookware. 💡 Halothane and other haloalkanes are still used as modern anaesthetics.

What is a Haloalkane?

A haloalkane is an organic compound in which one or more hydrogen atoms of an alkane are replaced by halogen atoms (F, Cl, Br, or I).

General formula: R-X

Where, **R** = alkyl group (e.g., $-\text{CH}_3$, $-\text{C}_2\text{H}_5$...) and **X** = halogen atom ($-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$)

Nature of C-X Bond

- Polar covalent bond Carbon: δ^+ , Halogen: δ^-

Since halogens are more **electronegative** than carbon, the shared electron pair is pulled towards the halogen atom. As a result, carbon becomes slightly positive (δ^+) and the halogen becomes slightly negative (δ^-).

Classification

A. Based on the Number of Halogen Atoms

- Monohaloalkanes $\rightarrow \text{CH}_3\text{Cl}$
- Dihaloalkanes $\rightarrow \text{CH}_2\text{Cl}_2$
- Trihaloalkanes $\rightarrow \text{CHCl}_3$
- Polyhaloalkanes $\rightarrow \text{CCl}_4$

B. Based on the Nature of the carbon atom

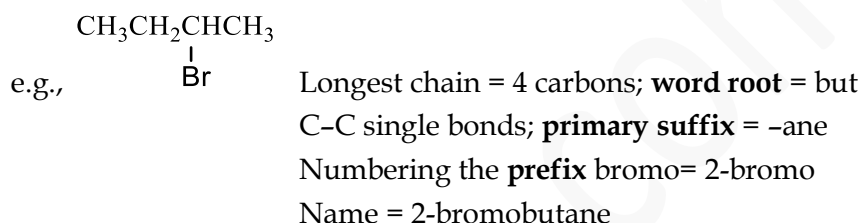
Type	Description	Example
Primary (1°)	Carbon attached to 1 carbon	CH ₃ CH ₂ Cl
Secondary (2°)	Attached to 2 carbons	CH ₃ CHClCH ₃
Tertiary (3°)	Attached to 3 carbons	(CH ₃) ₃ CCl

A **carbon bonded to only one** or no other carbon is called a **primary carbon**. A **carbon bonded to two other carbon** atoms is called **secondary**, and the **carbons bonded with 3 and 4 next carbon atoms** are respectively called **tertiary and quaternary** carbon atoms.

IUPAC and common nomenclature

IUPAC Rules

1. Select the longest carbon chain
2. Number the chain to give the substituent (halogen) the lowest possible locant.
3. Use prefixes: chloro-, bromo-, iodo-



Common Names

- Named as **alkyl + halide**

Example: CH₃Br → methyl bromide (IUPAC: bromomethane)

Bromoalkanes	IUPAC names	Common names	Class
CH ₃ Br	bromomethane	methyl bromide	1°
CH ₃ CH ₂ Br	bromoethane	ethyl bromide	1°
CH ₃ CH ₂ CH ₂ Br	1-bromopropane	n-propyl bromide	1°
$\begin{array}{c} \text{H}_3\text{C}-\text{CH}-\text{Br} \\ \\ \text{CH}_3 \end{array} \quad \begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_3 \\ \\ \text{Br} \end{array}$	2-bromopropane	isopropyl bromide	2°
CH ₃ CH ₂ CH ₂ CH ₂ Br (C ₄ H ₉ Br)	1-bromobutane	n-butyl bromide	1°
$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHCH}_3 \\ \\ \text{Br} \end{array} \quad (\text{C}_4\text{H}_9\text{Br})$	2-bromobutane	sec-butyl bromide	2°
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{CH}-\text{CH}_2-\text{Br} \end{array} \quad (\text{C}_4\text{H}_9\text{Br})$	1-bromo-2-methylpropane	isobutyl bromide	1°
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\ \\ \text{Br} \end{array} \quad (\text{C}_4\text{H}_9\text{Br})$	2-bromo-2-methylpropane	tert-butyl bromide	3°

 **Observe** the molecular formula of the last four compounds in the above table.

[2-chloropropane](#)

Isomerism

- Different **compounds having the same molecular formula** are called isomers.
- **Structural isomers** are compounds that **differ in structure** and have the same molecular formula.
- The following two types of structural isomerism are observed in monohaloalkanes.

Chain Isomerism (skeletal isomerism)

Chain isomers are compounds with the same molecular formula **differing only in the main carbon chain or skeleton**. Such isomerism is exhibited by haloalkanes having 4 or more carbon atoms.

e.g., 2-iodobutane and 2-iodo-2-methylpropane

Positional Isomerism

Position isomers are compounds with the same molecular formula **differing only in the position of the halo group**. Such isomerism is exhibited by haloalkanes having 3 or more carbon atoms.

e.g., 1-chloropropane and 2-chloropropane



Your Turn: Practice more examples of isomers with structure and names.



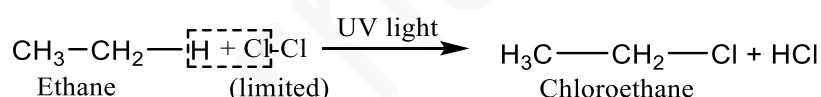
General Methods of Preparation of Monohaloalkanes (Alkyl halides)

Haloalkanes can be prepared from several organic compounds. The three methods included in the NEB syllabus are shown below.

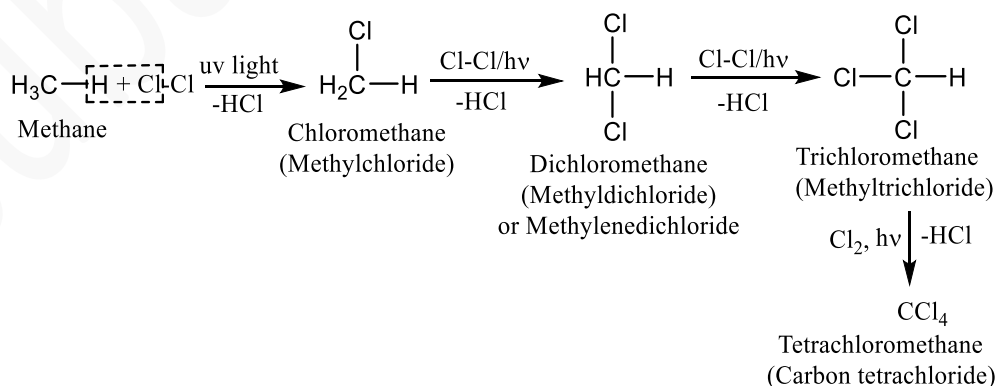
1. From Alkanes (by direct halogenation)

Alkanes undergo **free radical substitution** with halogens in the presence of UV light or sunlight.

Sunlight (UV light) provides the energy required for homolytic cleavage of the X-X bond, producing highly reactive free radicals that initiate the reaction. e.g.,

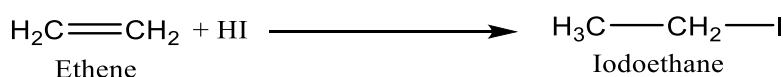


If chlorine is supplied in excess and the reaction is allowed to continue, all the hydrogen atoms may gradually be replaced by chlorine atoms.



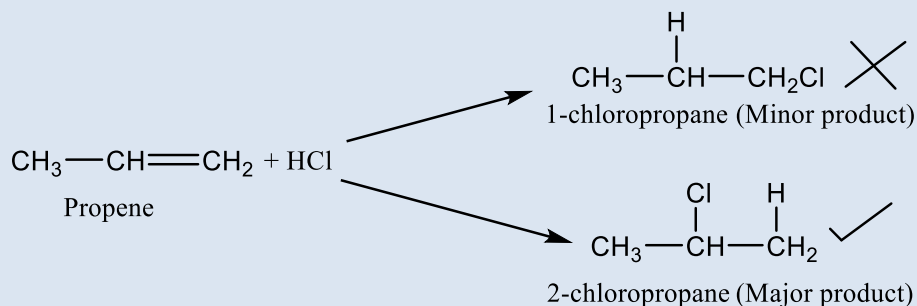
2. From Alkene (by hydrohalogenation)

Alkenes undergo **addition** with hydrohalic acids (HCl, HBr, and HI), yielding haloalkanes. e.g.,



Markovnikov's rule

When an unsymmetrical reagent adds to an unsymmetrical alkene, the positive part of the reagent (e.g., H^+) is attached to the carbon atom with more hydrogen atoms, and the negative part gets bonded to the carbon atom with a smaller number of hydrogen atoms. e.g.,

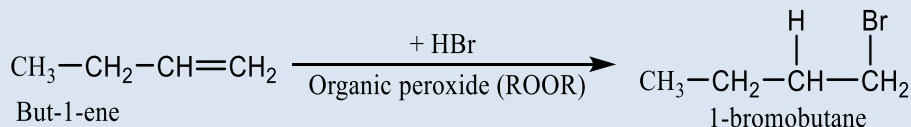


Why? The reaction proceeds mainly through the pathway that forms the **more stable carbocation intermediate**

 Memory Tip: Hydrogen goes to the carbon that already has more hydrogens.

Peroxide effect (Anti-Markovnikov's rule)

When HBr is added to unsymmetrical alkenes in the presence of organic peroxide, the positive part (H) gets bonded to the carbon having a smaller number of hydrogens, and the negative part (Br) gets bonded to the carbon having a higher number of hydrogens.

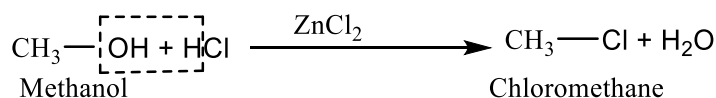


WHY? Only HBr has suitable bond energies to sustain the free-radical chain reaction required for the peroxide effect.

3. From alcohols

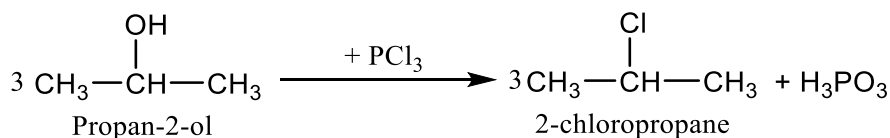
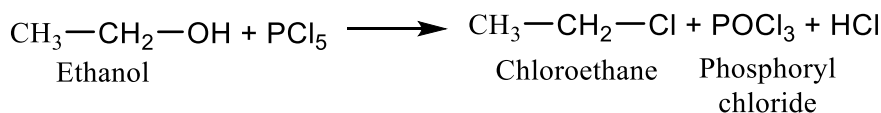
a. Reaction with halogen acids

- Alcohols, when treated with halogen acids (HCl, HBr, HI), have the -OH group replaced by the -X group (a halide).
- The reaction of alcohols with hydrochloric acid is slow; therefore, it requires ZnCl_2 as a catalyst. The mixture of conc. HCl and anhydrous ZnCl_2 is called **Lucas reagent**. e.g.,

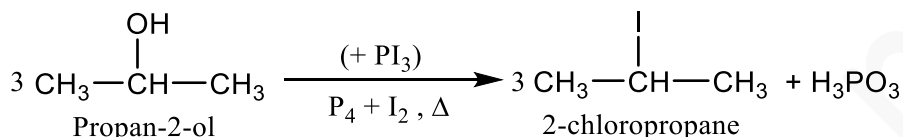


b. Reaction with $\text{PCl}_5/\text{PX}_3/\text{SOCl}_2$

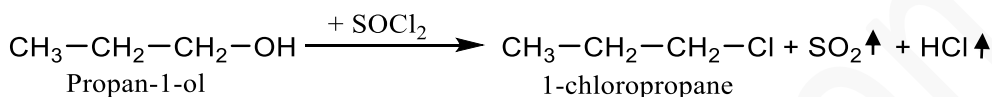
Alcohols react with PCl_5 , PCl_3 , and SOCl_2 , forming chloroalkanes. e.g.,



- Since PI_3 and PBr_3 are unstable, P_4 and I_2 or Br_2 are heated to produce PI_3 or PBr_3 in situ.



- SOCl_2 is a preferred reagent as the side products SO_2 and HCl escape as gases.



Preparations Summary:

Starting compound	Reagent	Reaction type
Alkane	Cl_2 / Br_2 + UV light	Substitution
Alkene	HCl / HBr / HI	Addition
Alcohol	HX , PCl_5 , SOCl_2	Substitution

Physical Properties

- Lower members - gases; higher members - liquids; even higher are waxy solids. Because the intermolecular force of attraction increases with increasing molecular mass.
- Boiling points increase with molecular mass in homologous series and among different halogen atoms. Again, due to increasing van der Waals' force with increasing molecular mass.
 $\text{R-I} > \text{R-Br} > \text{R-Cl}$
- Insoluble in water: due to their non-polar nature and inability to form hydrogen bonds.
Soluble in organic solvents like benzene, ether, and acetone.

Chemistry Around You

Dry-cleaning solvents such as perchloroethylene are halogenated organic compounds. Their low solubility in water but good ability to dissolve in oils makes them effective at removing grease and stains.

Chemical Properties

[A] Nucleophilic substitution reactions ($\text{S}_\text{N}1/\text{S}_\text{N}2$)

The most common type of reaction that haloalkanes undergo.

Occurs by replacing the halogen of the haloalkane with a nucleophile.

Its general form is expressed as



where Y^- is a nucleophile like OH^- , NH_2^- , CN^- , etc.

A nucleophile is an electron-rich species that attacks the electron-deficient carbon atom.

The nucleophilic substitution reactions are of two types, viz:

- S_{N}^1 (substitution nucleophilic unimolecular)
- S_{N}^2 (substitution nucleophilic bimolecular)

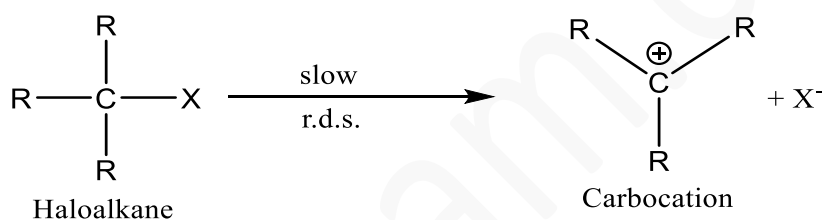
I) **S_{N}^1 reaction:** In this reaction, the rate of reaction depends upon the concentration of only one of the reactants, i.e., the haloalkane substrate. Hence called unimolecular.

Rate $\propto$ [Haloalkane]

Rate Law: Rate = $k[\text{R}-\text{X}]$

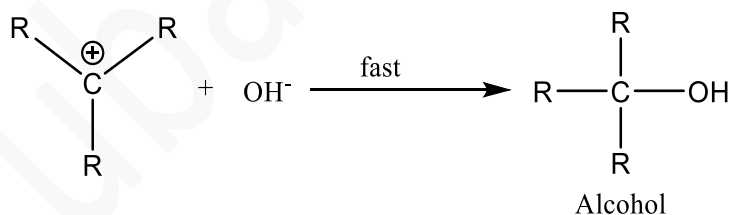
It is a two-step process.

Step I: Haloalkane undergoes heterolytic fission to form a **carbocation** and a halide ion. It's a slow, hence **rate-determining step** (r.d.s.).

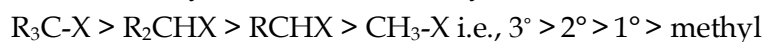


Hence, the rate can be expressed as: rate = k [Haloalkane]

Step II: The carbocation, being highly reactive, reacts with nucleophiles such as OH^- to form the product in a fast step.



The order of reactivity of 1° , 2° , 3° and methyl haloalkanes is in the following order;



Note

$\text{S}_{\text{N}}1$ is favoured by **tertiary haloalkanes** because the tertiary carbocation (3°) is the most stable (stabilised by three electron-donating alkyl groups).

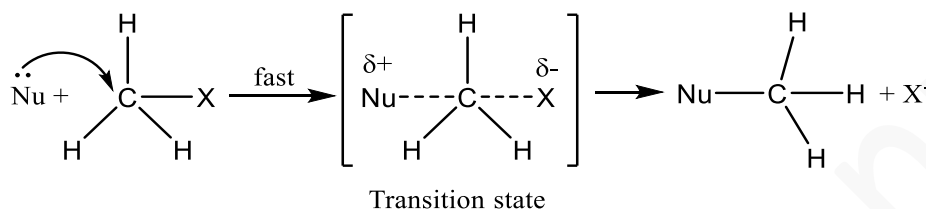
Stability of carbocations: $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$

II) S_N² reaction: This reaction occurs in a **single step**. The reaction rate depends on the concentrations of both the substrate (haloalkane) and the reagent (nucleophile). Hence, it is called a bimolecular reaction.

Rate law:

$$\text{Rate} = k [\text{R-X}] [\text{Nu}^-]$$

In the transition state, the nucleophile and the leaving group (halogen) are both partially bonded to the carbon atom.



The rate of reaction can be expressed as:

$$\text{Rate} = k [\text{haloalkane}] [\text{nucleophile}]$$

 **Note:** S_N² is favoured by **primary haloalkanes** there is less steric hindrance, allowing the nucleophile to approach the carbon atom more easily.

Primary halogenoalkanes tend to react via the S_N² mechanism; tertiary halogenoalkanes via the S_N¹ mechanism; and secondary halogenoalkanes via a mixture of the two, depending on structure.

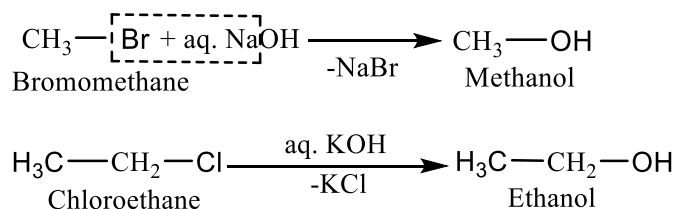
Quick comparison:

Feature	S _N ¹	S _N ²
Steps	Two (stepwise)	One (concerted)
Intermediate	Carbocation	None (transition state only)
Rate Law	Rate = k[R-X]	Rate = k[R-X][Nu ⁻]
Favoured by	Tertiary (3°) substrates	Primary (1°) substrates
Stereochemistry	Racemisation (mixture of enantiomers)	Inversion of configuration (Walden inversion)

www.youtube.com/watch?v=Bg3c5c9b1BQ&t=117s
[An Animated Explanation of Nucleophilic Substitution](#)

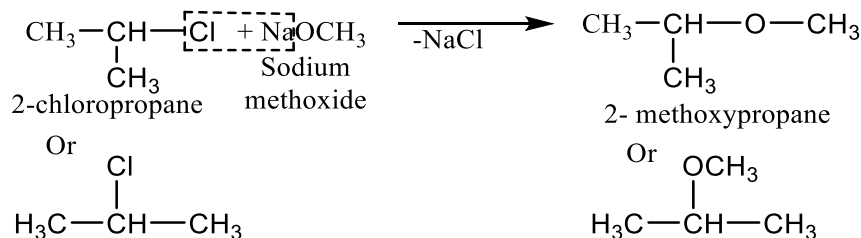
1. Formation of alcohols - Reaction with aqueous caustic alkali (substitution by -OH group)

When treated with aq. NaOH or KOH, haloalkanes give alcohols.



2. Formation of ether - Reaction with sodium or potassium alkoxide (substitution by -OR)(Williamson's etherification process)

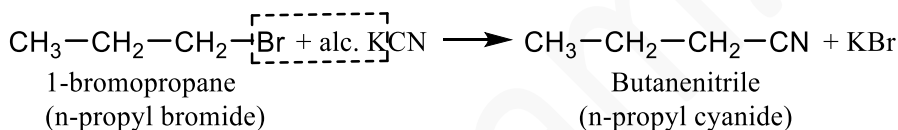
When treated with sodium alkoxide or potassium alkoxide, haloalkanes give ethers. This is a nucleophilic substitution reaction where the alkoxide ion (OR^-) acts as a nucleophile and substitutes the halogen atom from the alkyl halide.



 Importance of Williamson's ether synthesis

- It is an **S_N^2 reaction** of an alkoxide ion with a **primary alkyl halide** (or methyl halide).
- Helps to **prove the structure** of ethers.
- Suitable for preparing a **wide variety of symmetrical and unsymmetrical ethers**.

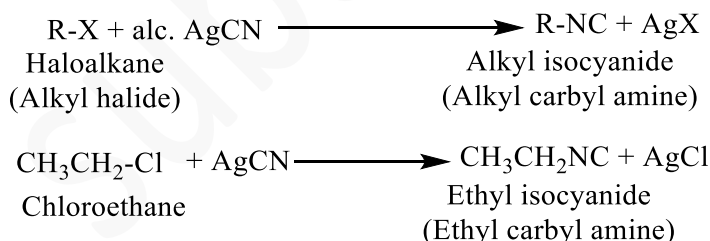
4. Formation of nitrile: Action of **alcoholic potassium cyanide** (substitution by -CN)



 **Note:** The chain length is increased by one carbon. CN^- is an **ambident** nucleophile — it can bond through C or through N.

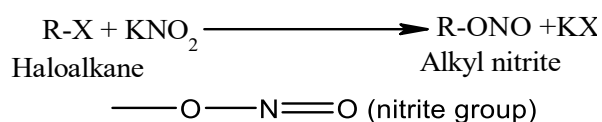
5. Formation of isocyanide (carbylamine): Reaction with alcoholic AgCN

Haloalkanes, when treated with **alc. AgCN**, give isocyanides.



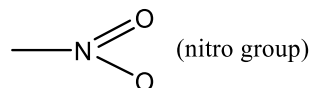
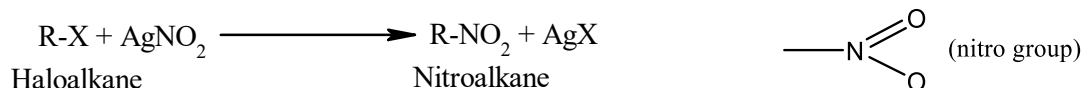
This occurs because CN^- is an **ambident** nucleophile and can attack through either carbon or nitrogen.

6. Formation of nitrites: action of alcoholic potassium nitrite



Reaction via the oxygen of NO_2^- (**ambident** nucleophile).

6. **Formation of nitro compound:** action of alcoholic silver nitrite

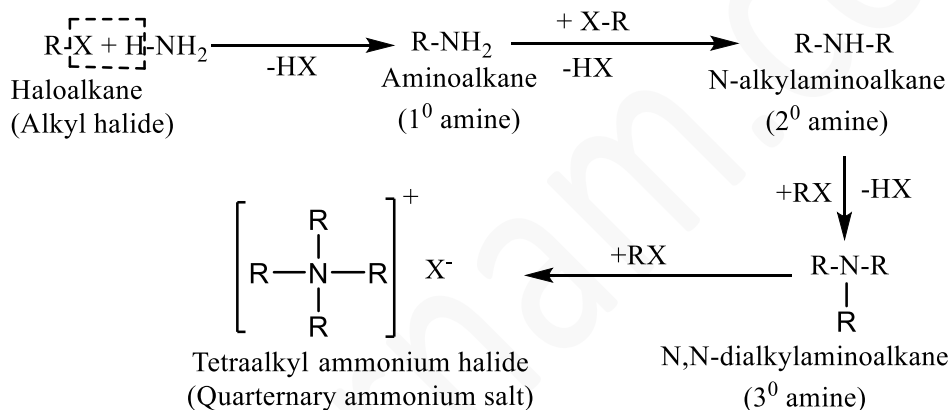


Due to the **ambident** nature of NO_2^- - may bond through N or O, depending on the reagent.

 **Note:** Reaction via the nitrogen of NO_2^- . AgNO_2 drives the reaction through N, giving a nitroalkane instead of a nitrite.

5. **Formation of amines:** Reaction with ammonia (Hoffmann's ammonolysis) - formation of different degrees of amines

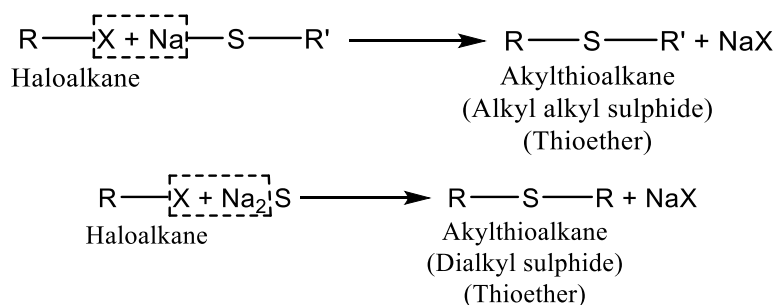
When an alkyl halide is heated with an aq. or an alcoholic solution of ammonia, a 1° amine is formed. Excess alkyl halide gives a mixture of primary, secondary, and tertiary amines, as well as quaternary ammonium salts.



 **Note:** Excess ammonia favours the primary amine. Excess alkyl halide gives a mixture of all degrees plus quaternary ammonium salt.

7. **Formation of thioether:**

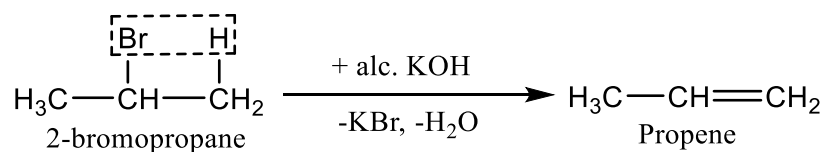
When alkyl halide is heated with Sodium or potassium sulphide in the presence of aqueous ethanol, a thioether is produced.



[B] Elimination Reaction

Dehydrohalogenation (reaction with alc. KOH)

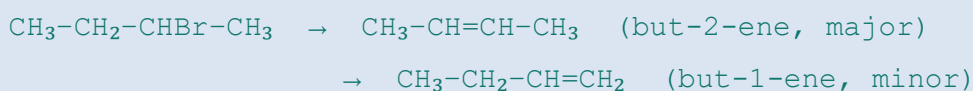
Haloalkanes undergo elimination with alcoholic KOH or NaOH, on heating, giving alkenes.



Saytzeff's Rule: When two different alkenes are possible from an elimination reaction, the alkene with the highest number of side chains (alkyl groups) is formed as a major product.

OR, the **more substituted alkene is the major product**

For example,



But-2-ene is more substituted $\rightarrow$ major product (Saytzeff's rule).

Competition: Substitution vs Elimination

- Aq. KOH/NaOH $\rightarrow$ substitution
- Alc. KOH/NaOH $\rightarrow$ elimination

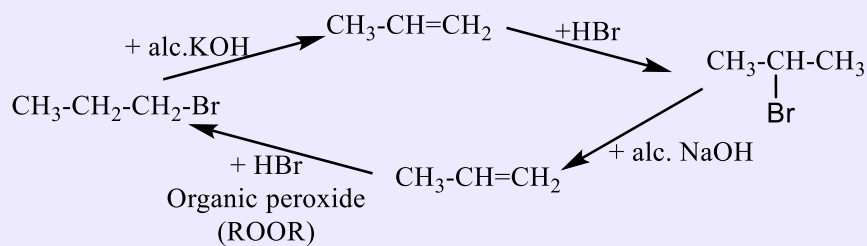


Worked Example 1

Convert 1-bromopropane to 2-bromopropane and vice versa.

2

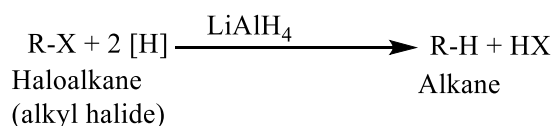
Solution:



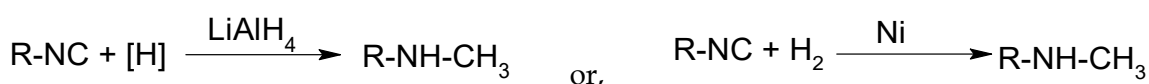
(Practice names and side products yourself.)

[C] Reduction

Haloalkanes are reduced to alkanes with lithium aluminium hydride, usually in dry ether.



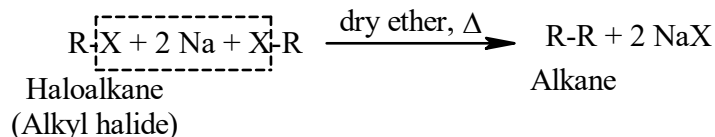
Isocyanides or carbyl amines also undergo reduction, giving 2° amines. This reaction is not particularly mentioned in the NEB syllabus but is asked frequently in the NEB exams.



[D] Reaction with metals

Wurtz reaction

Haloalkanes react with sodium metal **in the presence of dry ether**, a higher alkane in which two alkyl groups are joined together.

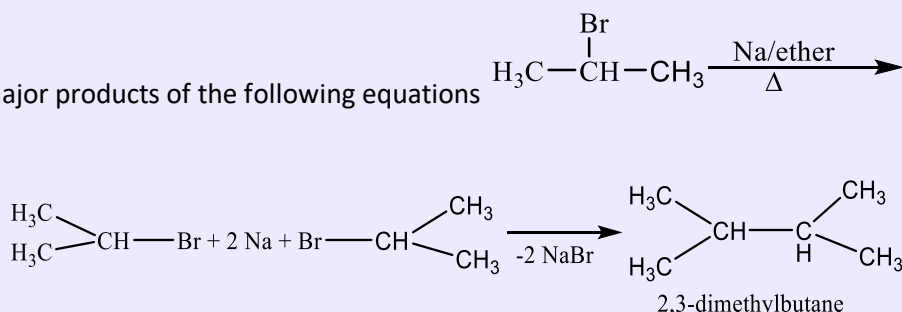


⚠ Limitation: If two different haloalkanes are used, three different alkanes are produced (a mixture), making the reaction less useful for synthesis.

Worked Example 2

Give the major products of the following equations

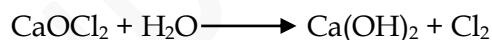
Solution:



Preparation of Chloroform

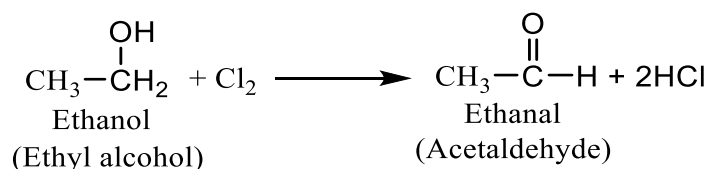
Chloroform is prepared in the laboratory by distilling ethanol (ethyl alcohol) or propanone (acetone) with an aqueous paste of bleaching powder. In the reaction, aqueous bleaching powder acts as an oxidising, chlorinating, and hydrolysing agent.

First, bleaching powder reacts with water,

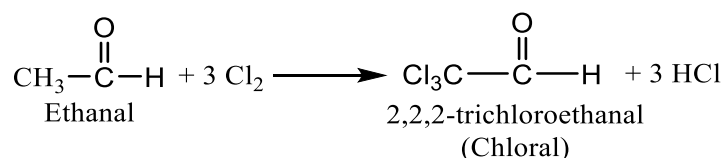


Preparation from ethyl alcohol involves the following steps-

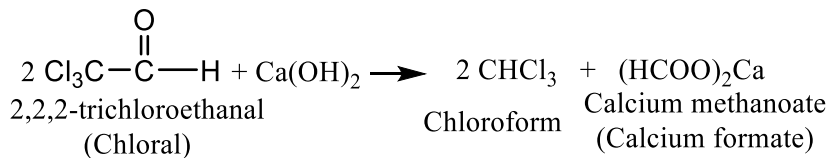
- **Oxidation** of ethyl alcohol into acetaldehyde:



- **Chlorination** of acetaldehyde into trichloroacetaldehyde (chloral)

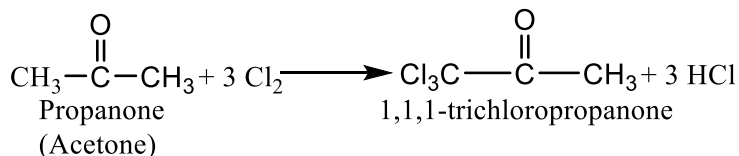


- **Hydrolysis** of chloral into chloroform.

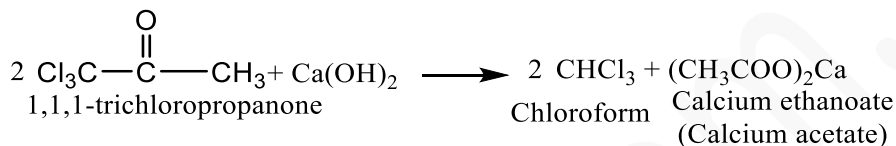


Preparation from propanone, similarly, involves only the following 2 steps-

- **Chlorination** of propanone into 1,1,1-trichloropropanone



- **Hydrolysis** of 1,1,1-trichloropropanone into chloroform.



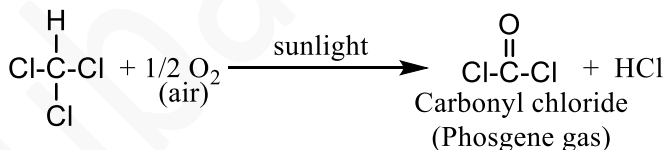
Properties of Trichloromethane

- It is a **sweet-smelling** colourless liquid. It is heavier than water with **sp. gr. 1.485**.
- It boils at 61 °C and freezes at -63 °C.
- It dissolves nonpolar compounds like fat, oil, and wax.
- If inhaled in a small amount, it causes temporary unconsciousness.

Inhalation of chloroform vapour can cause dizziness, nausea, and loss of consciousness; chloroform is toxic and should be handled carefully.

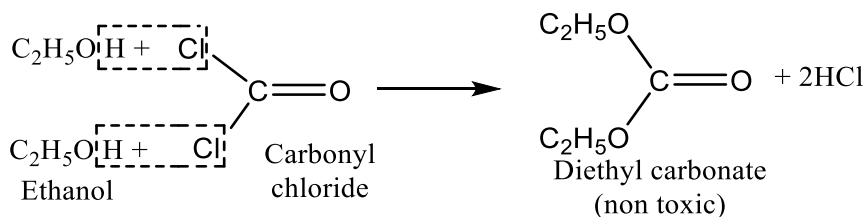
1) Oxidation - Reaction with air

When exposed to light and air, chloroform undergoes slow oxidation to form highly poisonous phosgene gas, which is highly toxic even at low concentrations. This is one reason why chloroform is no longer used as an anaesthetic.



So, to prevent the formation of carbonyl chloride, the following precautions should be taken.

- ✓ Store in a dark bottle to cut off the light.
- ✓ Fill the Chloroform up to the stopper to exclude air.
- ✓ 1% Ethanol is also added, which reacts with the phosgene gas formed and changes into a nontoxic compound- diethyl carbonate.

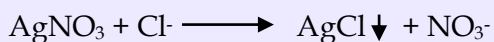


Worked Example

1. Why does chloroform not give a white precipitate with aqueous silver nitrate? 1

Solution: Chloroform and other chloroalkanes contain covalently bonded chlorine, which does not ionise easily in an aqueous solution. Therefore, they do not give a white precipitate with aqueous silver nitrate.

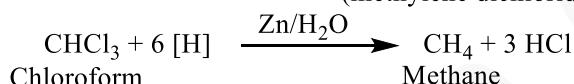
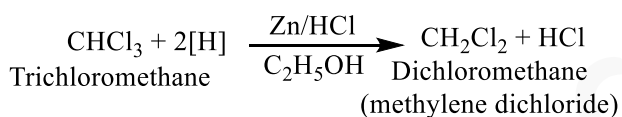
Unlike inorganic chlorides like NaCl, HCl, etc., which ionise into Cl⁻ (chloride ion), which reacts with AgNO₃, giving a white ppt. of AgCl.



[Note: But actually, chloroalkanes give a white ppt very slowly, like in an hour, due to hydrolysis]

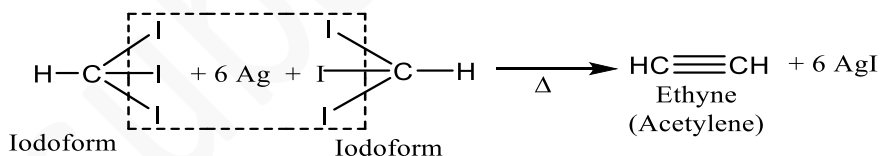
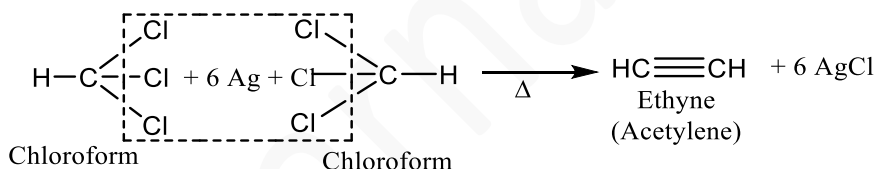
1) Reduction

Chloroform can be reduced to dichloromethane and methane, respectively, by Zn/HCl in the presence of ethanol and Zn dust in water.



2) Reaction with silver powder

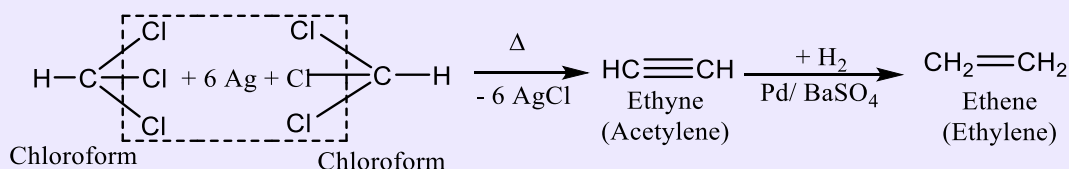
Chloroform and iodoform, when heated with silver powder, produce ethyne (acetylene).



Worked Example

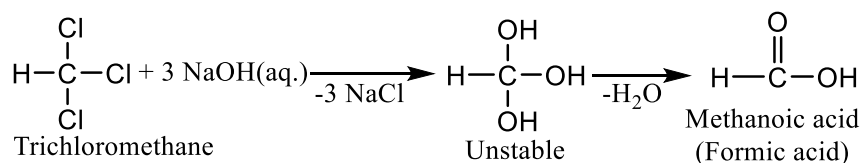
1. How would you obtain Ethylene from Trichloromethane?

Solution:



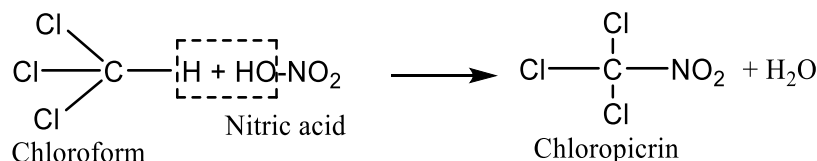
3) Reaction with aqueous caustic alkali (Hydrolysis)

Chloroform reacts with aqueous NaOH or KOH to form an unstable intermediate, which decomposes to give formate (methanoate) ions. Methanoic acid is obtained after acidification.



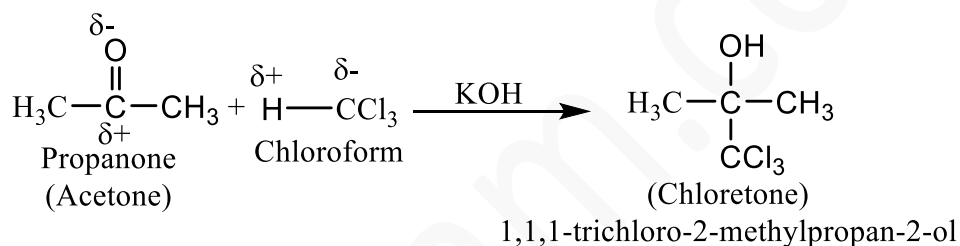
4) Reaction with concentrated HNO₃

Chloroform reacts with conc. nitric acid to form chloropicrin. Chloropicrin is used as a broad-spectrum *antimicrobial, fungicide, herbicide, insecticide*, and a component of tear gas.



5) Reaction with Propanone (acetone)

Chloroform condenses with propanone (acetone) in the presence of KOH to give chloretone, which is used as a hypnotic drug (sleep-inducing).



Chapter — Summary

Topic	Key Points
Preparation	(1) Alkane + X ₂ /hν → haloalkane (free radical substitution) (2) Alkene + HX → haloalkane (Markovnikov's rule) (3) Alcohol + HX/PX ₃ /SOCl ₂ /PCl ₅ → haloalkane
S_N1	Two steps; carbocation; rate = k[R-X]; favoured by 3° R-X
S_N2	One step; no intermediate; rate = k[R-X][Nu ⁻]; favoured by 1° R-X
Substitution products	Alcohols, ethers, nitriles, isocyanides, nitrites, nitroalkanes, amines, thioethers
Elimination	Alc. KOH → alkene; major product = more substituted alkene (Saytzeff's rule)
Reduction	LiAlH ₄ , dry ether → alkane
Wurtz reaction	2R-X + 2Na → R-R + 2 NaX; doubles the carbon chain
Chloroform prep	Ethanol or propanone + bleaching powder + water (distillation)
Chloroform oxidation	Air + light → phosgene (toxic); prevent by dark bottle + 1% ethanol