# 8. HALOALKANES (ALKYL HALIDES)



**🎯 Learning outcomes**

by the end of the chapter, 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 physical properties of haloalkanes.
4. Describe chemical properties of haloalkanes: substitution reactions, $SN^1$ and $SN^2$ reactions (basic concept only).
5. Explain the formation of alcohol, nitrile, amine, ether, thioether, carbylamines, nitrite, and nitroalkane using haloalkanes
6. Describe elimination reactions (dehydrohalogenation- 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 form the backbone of many drugs, refrigerants, and solvents. 🌾 Many pesticides contain haloalkanes. 🍳 Teflon (polytetrafluoroethylene) 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., $–CH_3$, $–C_2H_5$ …) and **X** = halogen atom (–F, –Cl, –Br, –I)

**Nature of C–X Bond**

- Polar covalent bond  Carbon: $\delta^+$, Halogen: $\delta^-$

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

### Classification

**A. Based on the Number of Halogen Atoms**

- **Mono**haloalkanes → $CH_3Cl$
- **Di**haloalkanes → $CH_2Cl_2$
- **Tri**haloalkanes → $CHCl_3$
- **Poly**haloalkanes → $CCl_4$

**B. Based on the Nature of the carbon atom**

| Type | Description | Example |
|---|---|---|
| Primary (1°) | Carbon attached to 1 carbon | $CH_3CH_2Cl$ |
| Secondary (2°) | Attached to 2 carbons | $CH_3CHClCH_3$ |
| Tertiary (3°) | Attached to 3 carbons | $(CH_3)_3CCl$ |

A **carbon bonded with only one or no other carbon** is called a **primary carbon**. The **carbon bonded with the two next 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 halogen the lowest position
3. Use prefixes: chloro-, bromo-, iodo-

e.g., $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$

Longest chain = 4 carbons; **word root** = but
C-C single bonds; **primary suffix** = ane
Numbering the **prefix** bromo= 2-bromo
Name = 2-bromobutane

### Common Names

- Named as **alkyl + halide**
  Example: $CH_3Br$ → methyl bromide (IUPAC: bromomethane)

| Bromoalkanes | IUPAC names | Common names | Degree |
|---|---|---|---|
| $CH_3Br$ | Bromomethane | Methyl bromide | $1^0$ |
| $CH_3CH_2Br$ | Bromoethane | Ethyl bromide | $1^0$ |
| $CH_3CH_2CH_2Br$ | 1-bromopropane | n-propyl bromide | $1^0$ |
| $H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-Br$ $CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$ | 2-bromopropane | iso-propyl bromide | $2^0$ |
| $CH_3CH_2CH_2CH_2Br$ **($C_4H_9Br$)** | **1-bromobutane** | **n-butyl bromide** | $1^0$ |
| $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$ **($C_4H_9Br$)** | **2-bromobutane** | **sec-butyl bromide** | $2^0$ |
| $H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-Br$ **($C_4H_9Br$)** | **1-bromo-2-methylpropane** | **iso-butyl bromide** | $1^0$ |
| $H_3C-\underset{\displaystyle Br}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$ **($C_4H_9Br$)** | **2-bromo-2-methylpropane** | **tert-butyl bromide** | $3^0$ |

🧠 **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

[Practice more examples of isomers with structure and names.]

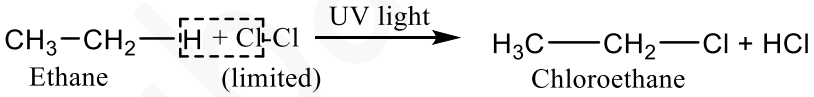
## General Methods of Preparation of Monohaloalkanes (Alkyl halides)

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

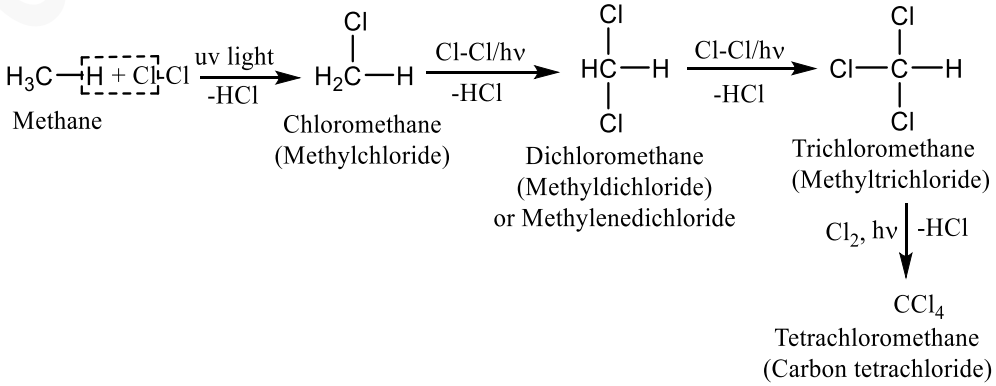
### 1. From Alkanes (by direct halogenation)

Alkanes can be halogenated easily in the presence of sunlight (UV light). These reactions are free radical substitution reactions.

Sunlight (UV light) provides the energy needed to break the X–X bond, producing highly reactive free radicals that initiate the reaction. e.g.,

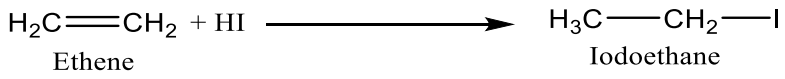



If chlorine is supplied in excess and the reaction is allowed to continue, all the hydrogen atoms may gradually be replaced by chlorine atoms.



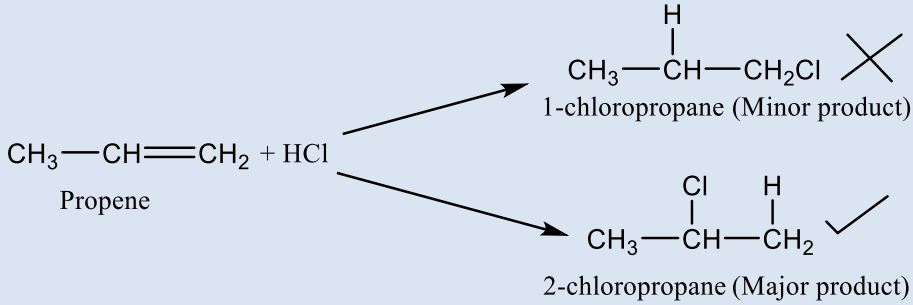
## 2. From Alkene (by hydrohalogenation)

Alkenes undergo **addition** with hydrohalic acids (HCl, HBr, and HI), resulting in 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.,

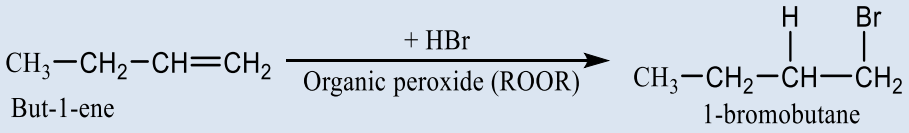



**Why?** It operates because the reaction follows the pathway that forms the **more stable carbocation intermediate**

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 with the carbon having a smaller number of hydrogens, and the negative part (Br) gets bonded with the carbon having a higher number of hydrogens.

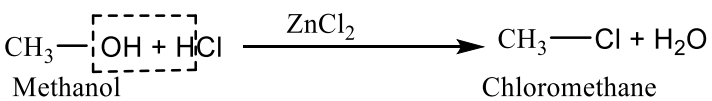



**WHY?** Only HBr has suitable bond energies to sustain the free-radical chain reaction required for the peroxide effect.

## 3. From alcohols

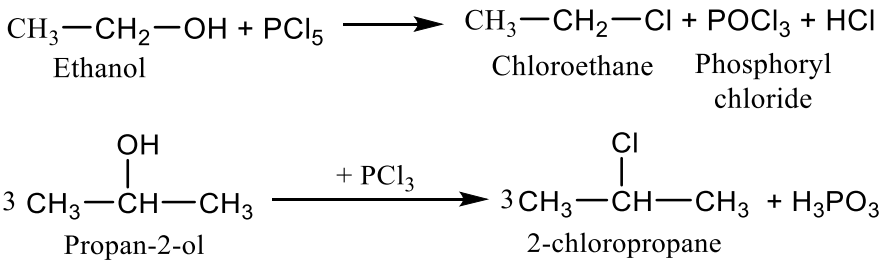
### a. Reaction with halogen acids

- Alcohols, when treated with halogen acids (HCl, HBr, HI), the -OH group is substituted with the -X group (halide).
- The reaction of alcohols with hydrochloric acid is slow; therefore, it requires the presence of $ZnCl_2$ as a catalyst. e.g.,

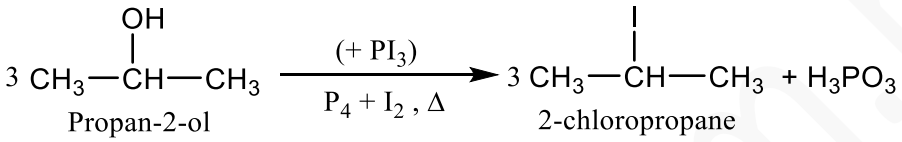


b. **Reaction with $PCl_5/PX_3/SOCl_2$**

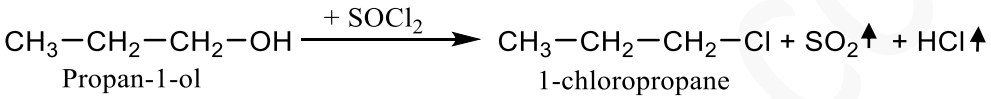
Alcohols also react with $PCl_5$, $PCl_3$, and $SOCl_2$, forming Chloroalkanes. e.g.,




- **In the case of $PI_3$ and $PBr_3$, being unstable, $P_4$ and $I_2$ or $Br_2$ are heated to produce the $PI_3$ or $PBr_3$ <u>in situ</u>.**




- **$SOCl_2$ 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 with a pleasant smell; even higher are waxy solids. Because the intermolecular force of attraction increases with increasing molecular mass.
- Boiling points increase with the molecular masses in homologous series and among different halogen atoms. Again, due to increasing van der Waals' force with increasing molecular mass.
  RI > RBr > RCl
- 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 haloalkanes. Their poor solubility in water but good solubility in oils makes them effective at removing grease and stains.

## [A] Nucleophilic substitution reactions ($SN^1/SN^2$)

The most common type of reaction that Haloalkanes undergo.

occur 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 positively charged carbon atom.

The nucleophilic substitution reactions are of two types, viz:

i) $SN^1$ (substitution nucleophilic unimolecular)
ii) $SN^2$ (substitution nucleophilic bimolecular)

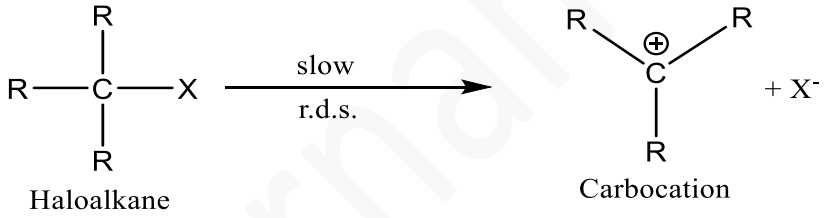
I) **$SN^1$ reaction:** In this reaction, the rate of reaction depends upon the concentration of only one of the reactants, i.e., the haloalkane substrate. Hence called unimolecular.

Rate ∝ [Haloalkane]

**Rate Law:** Rate = k[R−X]

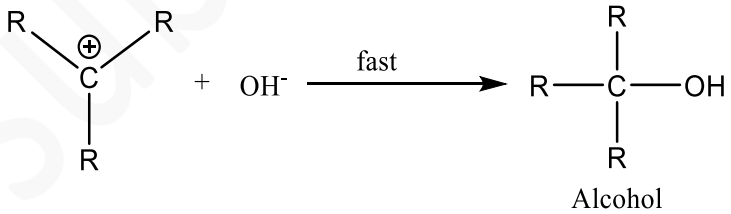
It is a two-step process.

**Step I:** Haloalkane undergoes heterolytic fission to form a **carbocation** and a halide ion. It's a slow, hence **r**ate-**d**etermining **s**tep(rds).




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 $1^0, 2^0, 3^0$ and methyl haloalkanes is in the following order;

$R_3C\text{-}X > R_2CHX > RCHX > CH_3\text{-}X$ i.e., $3^0 > 2^0 > 1^0 >$ methyl

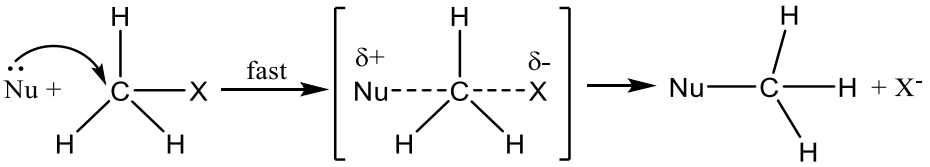
> **Note**
>
> $S_n1$ is favoured by **tertiary haloalkanes** because the tertiary carbocation (3°) is the most stable (stabilised by three electron-donating alkyl groups).
>
> Stability of carbocations: $3^\circ > 2^\circ > 1^\circ > CH_3^+$

**II)** **$SN^2$ reaction:** This reaction occurs in a **single step**. The rate of the reaction depends on the concentration of both the substrate (haloalkane) and the reagent (nucleophile). Hence, it is called a bimolecular reaction.

**Rate law:**

Rate = k [R−X] [$Nu^-$]

In the transition state, the nucleophile and the leaving group (halogen) have partial bonds.




Transition state

The rate of reaction can be expressed as:

Rate = k [haloalkane] [nucleophile]

> **Note** $S_n2$ is favoured by **primary haloalkanes** — there is less steric hindrance, so the nucleophile can approach easily.

Primary halogenoalkanes tend to react via the $SN^2$ mechanism; tertiary halogenoalkanes via the $SN^1$ mechanism; and secondary halogenoalkanes by a mixture of the two, depending on structure.

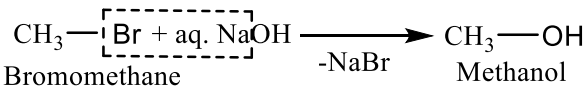
Quick comparison:

| Feature | $S_n1$ | $S_n2$ |
|---|---|---|
| **Steps** | Two (stepwise) | One (concerted) |
| **Intermediate** | Carbocation | None (transition state only) |
| **Rate Law** | k[R–X] | k[R–X][$Nu^-$] |
| **Favoured by** | Tertiary (3°) substrates | Primary (1°) substrates |
| **Stereochemistry** | Racemisation (mixture of products) | Inversion of configuration (Walden inversion) |

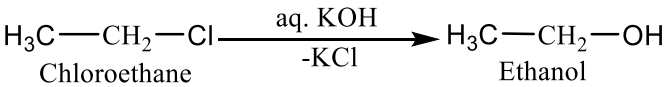
www.youtube.com/watch?v=Bg3c5c9b1BQ&t=117s
An Animated Explanation of Nucleophilic Substitution

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

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



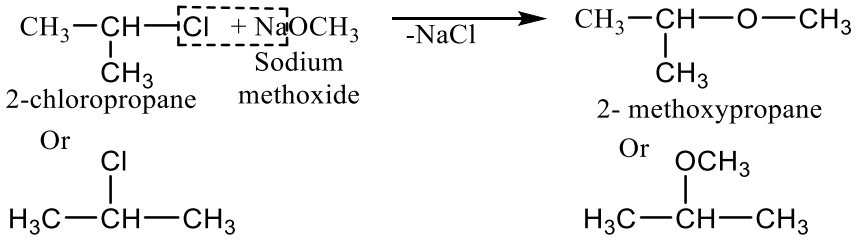

Bromomethane — Methanol




Chloroethane — Ethanol

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

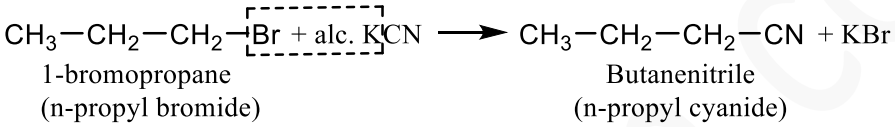
When treated with sodium alkoxide or potassium alkoxide, haloalkanes give ethers. This is a nucleophilic substitution reaction where the alkoxide ion ($OR^-$) acts as a nucleophile and substitutes the halogen atom from the alkyl halide.




**Importance of Williamson's etherification**

- It is an **$SN^2$ reaction** of an alkoxide ion with **a primary alkyl 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.

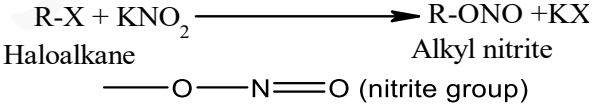
**5. Formation of carbyl amine**(isocyanide): Reaction with alcoholic AgCN

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



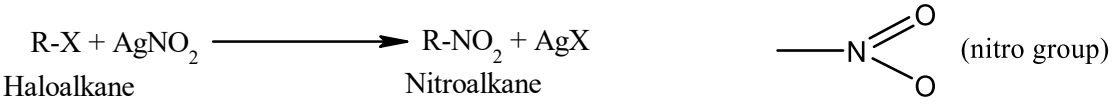
Due to the ambident nature of $CN^-$.

**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

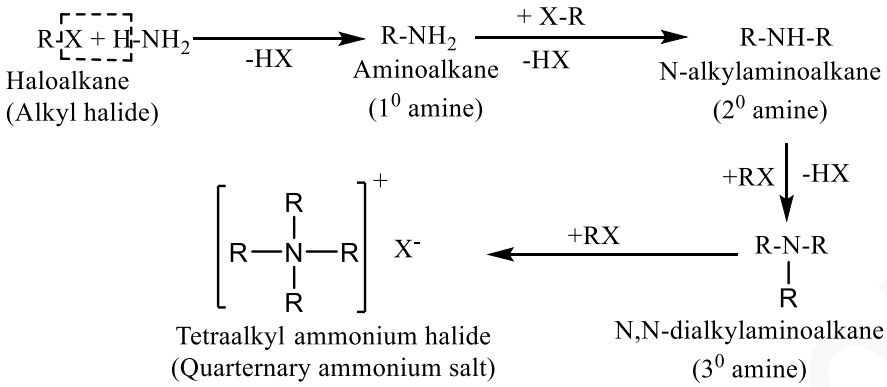



Due to the ambident nature of $NO_2^-$.

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

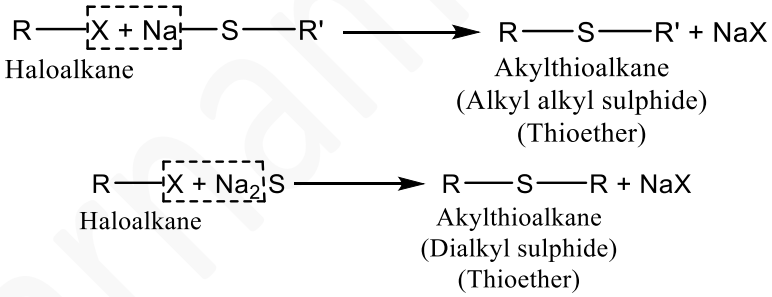
**5. Formation of amines**: Reaction with ammonia (Hoffmann's ammonolysis) - formation of different degrees of amines

When an alkyl halide is heated with an aq or an alcoholic solution of ammonia, a $1^0$ amine is formed. Excess of alkyl halide gives a mixture of primary, secondary, and tertiary amines and quaternary ammonium salts.




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

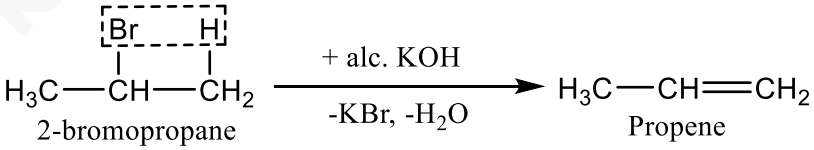
**7. Formation of thioether:** (action of thioalcohol)




## [B] Elimination Reaction

**Dehydrohalogenation** (reaction with alc. KOH)

Haloalkanes undergo elimination with alcoholic KOH or NaOH, 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,**

$CH_3-CH_2-CHBr-CH_3 \rightarrow CH_3-CH=CH-CH_3$ (but-2-ene, major)

$\rightarrow CH_3-CH_2-CH=CH_2$ (but-1-ene, minor)

*But-2-ene is more substituted → major product (Saytzeff's rule).*

**Competition: Substitution vs Elimination**

- **Aq. KOH/NaOH → substitution**
- **Alc. KOH/NaOH → elimination**

## [C] Reduction

Haloalkanes are reduced to alkanes with lithium aluminium hydride.

$$\underset{\text{Haloalkane (alkyl halide)}}{\text{R-X + 2 [H]}} \xrightarrow{LiAlH_4} \underset{\text{Alkane}}{\text{R-H + HX}}$$

## [D] Reaction with metals

**Wurtz reaction**

Haloalkanes react with sodium metal **in the presence of dry ether**, forming an **alkane with a double number of carbon** atoms.

$$\underset{\text{Haloalkane (Alkyl halide)}}{\text{R-X + 2 Na + X-R}} \xrightarrow{\text{dry ether, } \Delta} \underset{\text{Alkane}}{\text{R-R + 2 NaX}}$$

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

## 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,

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

Preparation from ethyl alcohol involves the following steps-

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

$$\underset{\text{Ethanol (Ethyl alcohol)}}{CH_3-CH_2-OH} + Cl_2 \longrightarrow \underset{\text{Ethanal (Acetaldehyde)}}{CH_3-C(=O)-H} + 2HCl$$

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

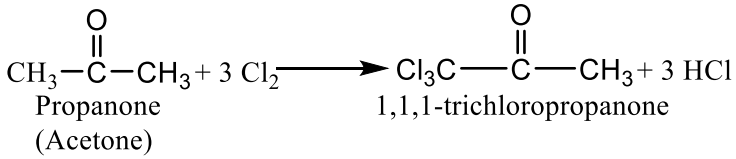
$$\underset{\text{Ethanal}}{CH_3-C(=O)-H} + 3\,Cl_2 \longrightarrow \underset{\text{2,2,2-trichloroethanal (Chloral)}}{Cl_3C-C(=O)-H} + 3\,HCl$$

- **Hydrolysis** of chloral into Chloroform.

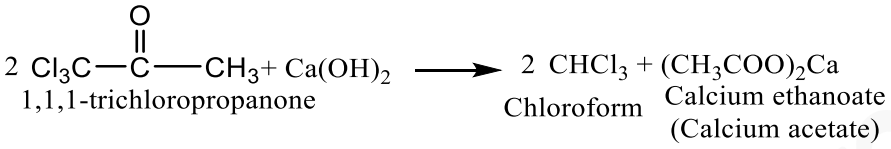
$$\underset{\text{2,2,2-trichloroethanal (Chloral)}}{2\,Cl_3C-C(=O)-H} + Ca(OH)_2 \longrightarrow \underset{\text{Chloroform}}{2\,CHCl_3} + \underset{\text{Calcium methanoate (Calcium formate)}}{(HCOO)_2Ca}$$

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.

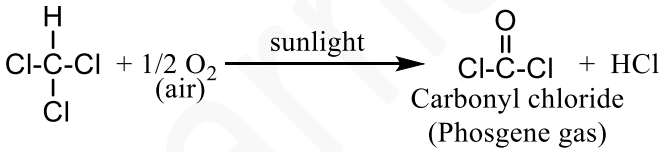



## Properties of Trichloromethane

- 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 $^0$C.
- It dissolves nonpolar compounds like fat, oil, and wax.
- If inhaled in a small amount, it causes temporary unconsciousness.

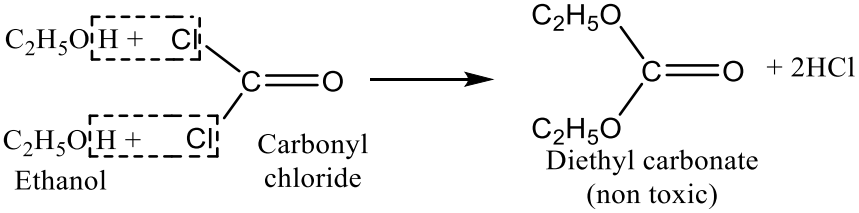
### 1) Oxidation - Reaction with air

When exposed to light and air, chloroform undergoes slow oxidation to give highly poisonous phosgene gas, which can cause death in higher amounts. This is one of the reasons for discarding Chloroform 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 $AgNO_3$, giving a white ppt. of AgCl.

$$AgNO_3 + Cl^- \longrightarrow AgCl\downarrow + NO_3^-$$

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

## 1) Reduction

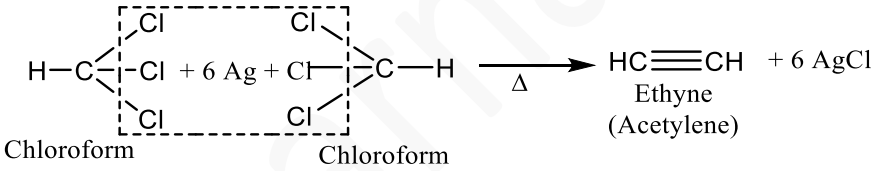
Chloroform can be reduced to Dichloromethane and Methane, respectively, by Zn/HCl in the presence of Ethanol and Zn dust in water.

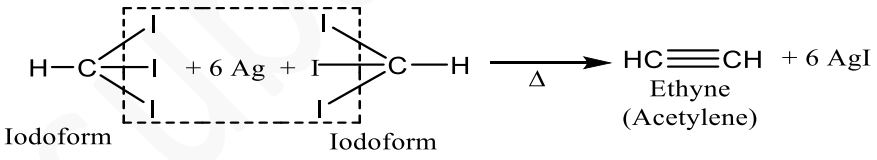
$$\underset{\text{Trichloromethane}}{CHCl_3} + 2[H] \xrightarrow[C_2H_5OH]{Zn/HCl} \underset{\text{Dichloromethane (methylene dichloride)}}{CH_2Cl_2} + HCl$$

$$\underset{\text{Chloroform}}{CHCl_3} + 6\,[H] \xrightarrow{Zn/H_2O} \underset{\text{Methane}}{CH_4} + 3\,HCl$$

## 2) Reaction with silver powder

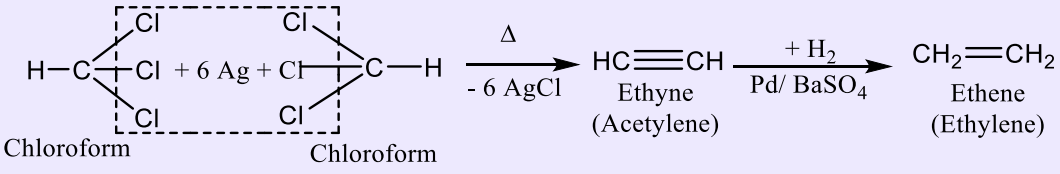
Chloroform and Iodoform both, when heated with silver powder, give Ethyne (Acetylene).



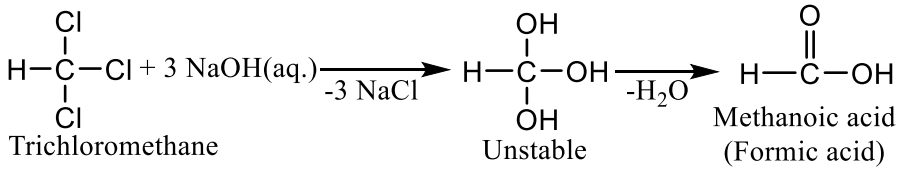

**Worked Example**

1. How would you obtain Ethylene from Trichloromethane?



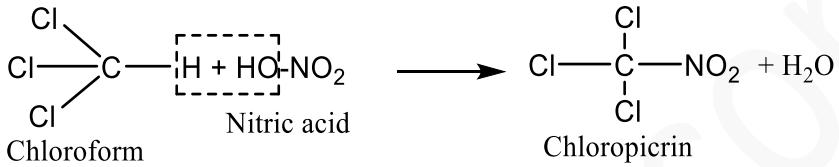
3) **Reaction with aqueous Caustic alkali** (Hydrolysis)

Chloroform reacts with aqueous NaOH or KOH, forming a tri-alcohol, which is a typical substitution reaction like that of monohaloalkanes. But the triol, being very unstable, undergoes decomposition, losing a molecule of water and resulting in Methanoic acid.



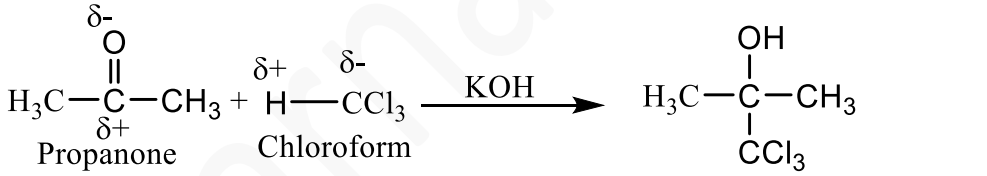

**4) Reaction with concentrated $HNO_3$**

Chloroform reacts with conc. Nitric acid, resulting in 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 + $X_2$/hv (2) Alkene + HX (Markovnikov) (3) Alcohol + $HX/PX_3/SOCl_2$ |
| **$S_n1$** | 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) |
| **Reduction** | $LiAlH_4$ / dry ether → alkane |
| **Wurtz reaction** | 2R–X + 2Na → R–R; 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 |



***...***