

# Alkyl Halides & Alcohols

**B. Pharm. I Year II Sem. (As per PCI)**



## Alkyl Halides

- SN1 and SN2 reactions,
- SN1 versus SN2 reactions,
- Factors affecting SN1 & SN2
- Structure and uses

## Alcohols

- Quality Test for Alcohols
- Structure and uses alcohols

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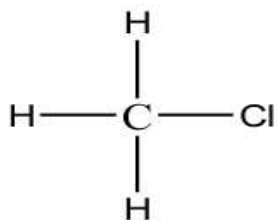
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# Alkyl Halides / Haloalkanes

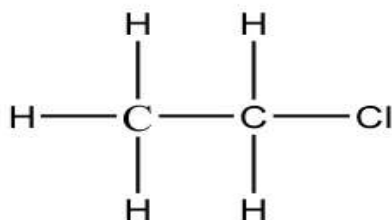
Alkyl halides are also known as **haloalkanes**.

Alkyl halides are compounds in which **one or more hydrogen atoms in an alkane have been replaced by halogen atoms** (fluorine, chlorine, bromine or iodine).

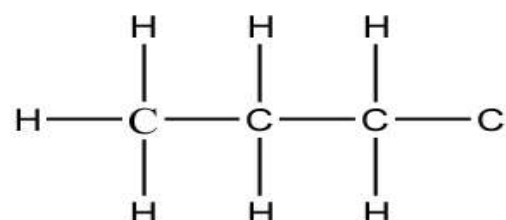
Alkyl halides are represented by **R-X** (Where R-alkyl group, X- F, Cl, Br or I)



Methyl chloride



ethyl chloride



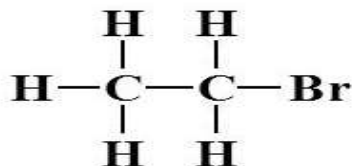
propyl chloride

## Types of Organic Halides:

**Alkyl Halides:** Have a halogen atom (X) bonded to a C-C Bond.

**Vinyl Halides:** Have a halogen atom (X) bonded to a C=C Bond.

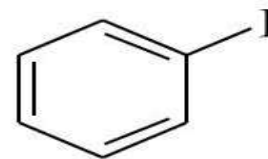
**Aryl Halides:** Have a halogen atom (X) bonded to a Ar-C Bond.



alkyl halide



vinyl halide



aryl halide

# Classification for Alkyl Halides

The number of alkyl groups attached to the carbon to which the halogen is bonded determines whether an alkyl halide is Primary, Secondary or Tertiary.

**Primary (1°) Alkyl Halides:** have one R group attached to the carbon linked to the halogen.

**Secondary (2°) Alkyl Halides:** have two R groups attached to the carbon linked to the halogen.

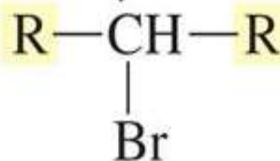
**Tertiary (3°) Alkyl Halides:** have three R groups attached to the carbon linked to the halogen.

a primary carbon



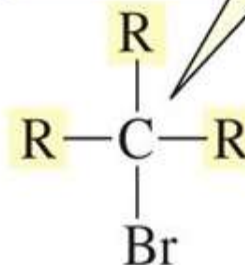
a primary alkyl halide

a secondary carbon



a secondary alkyl halide

a tertiary carbon



a tertiary alkyl halide

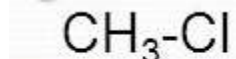
# Nomenclature of Alkyl Halides

Alkyl Halides are named in two ways:

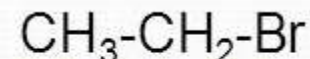
## 1) Common System:

In this system the alkyl group attached to the halogen atom is named first.

**Note:** The common names of alkyl halides are **TWO-WORD** names.



Methyl Chloride



Ethyl bromide

## 2. IUPAC System:

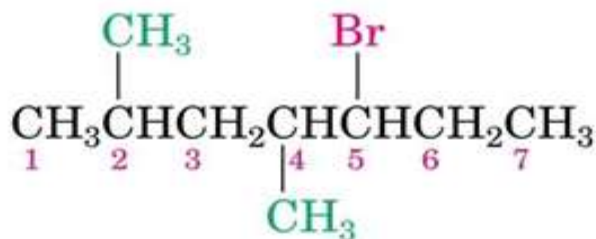
a. **Select the longest carbon** chain containing the halogen atom.

b. **Number the carbons** of the parent chain beginning at the end nearer the first substituent, whether alkyl or halo.

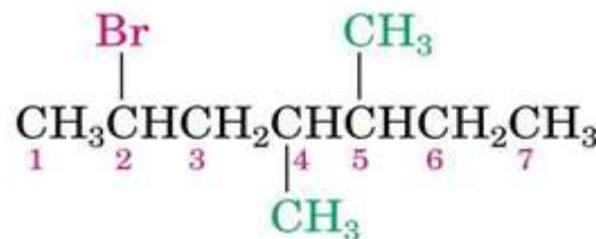
c. If more than one of the same kind of halogen is present, use prefix **di, tri, tetra**.

d. If there are several different halogens, number them and list them in **alphabetical order**

**Note:** The IUPAC names of alkyl halides are **ONE -WORD** names



**5-Bromo-2,4-dimethylheptane**



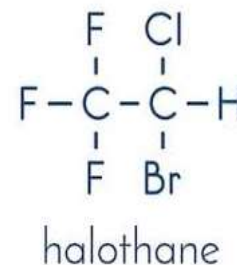
**2-Bromo-4,5-dimethylheptane**

# Physical Properties

- ✚ **Solubility** : All organic halides are insoluble in water and soluble in common organic solvents.
- ✚ **Boiling point** : The boiling points increases with increasing in molecular weights.
- ✚ Therefore, the boiling points increases in the order  $F < Cl < Br < I$
- ✚ **Electronegativities order**:  $F > Cl > Br > I$
- ✚ **Bond lengths order**:  $C-F < C-Cl < C-Br < C-I$
- ✚ **Alkyl halides are weak polar molecules**
- ✚ **Density correspond to the molecular weight** – Density order  $F < Cl < Br < I$

## Uses of Alkyl Halides:

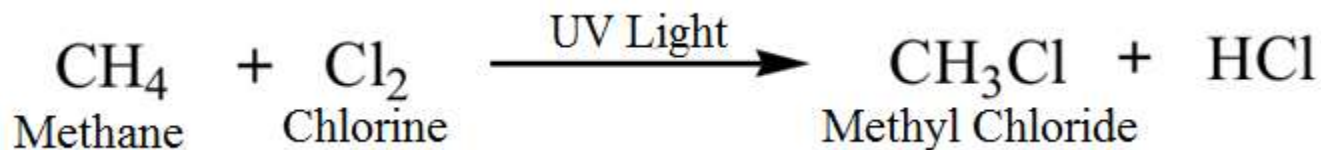
- ✚ **Solvents** - degreasers and dry cleaning fluid
- ✚ **Reagents** for synthesis of other compounds
- ✚ **Anesthetic**: Halothane is  $CF_3CHClBr$
- ✚  $CHCl_3$  used originally (toxic and carcinogenic)
- ✚ Freons, chlorofluorocarbons or CFC's Freon 12,  $CF_2Cl_2$ , now replaced with Freon 22,  $CF_2CHCl$ , not as harmful to ozone layer.
- ✚ **Pesticides** - DDT banned in U.S.



# Preparation of Alkyl Halides

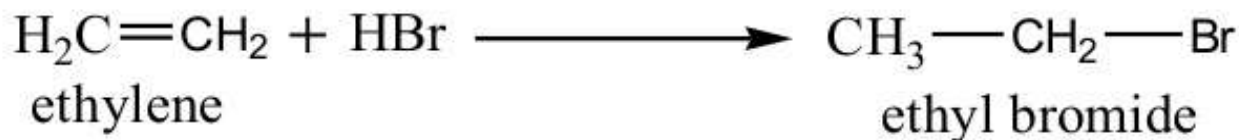
## Halogenation of Alkanes:

It involves substitution of H-atoms of Alkanes by as many halogens (Cl, Br, F & I). Methane reacts with chlorine in the presence of **UV light or at high temp. (300°C)** to yield methyl chloride.



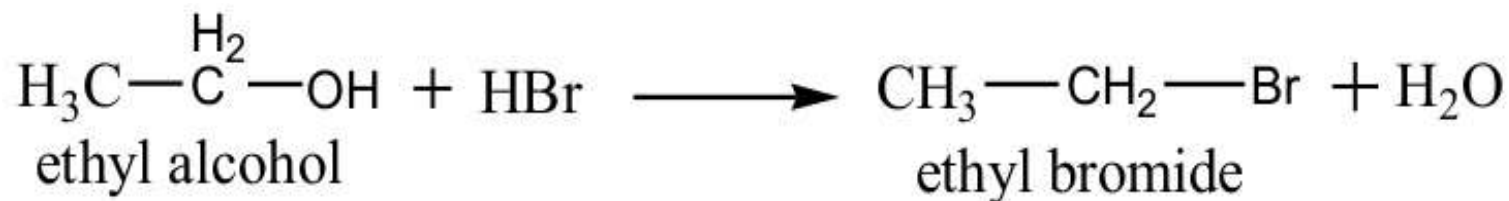
## Addition of Halogen Acids to Alkenes:

Alkenes reacts with hydrogen halides (HCl, HBr & HI) to form Alkyl Halides.



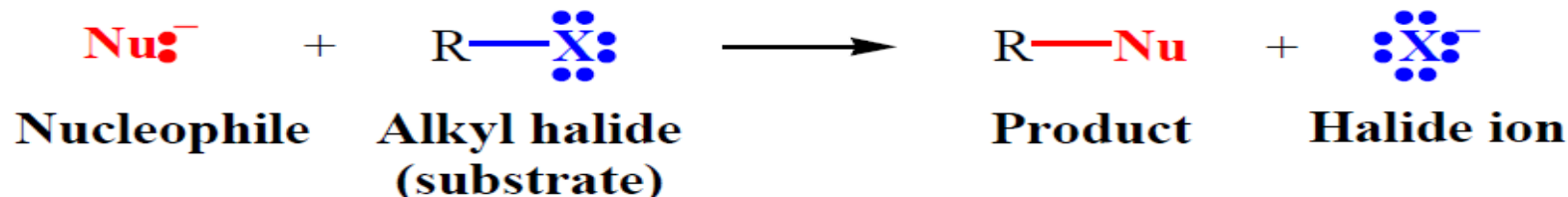
## Action of Halogen Acids on Alcohol:

Alcohol reacts with HBr or HI to produce Alkyl Halides.



# Nucleophilic Substitution Reactions (SN1 and SN2)

A nucleophile, a species with an unshared electron pair (lone-pair electrons), reacts with an alkyl halide (substrate) by replacing the halogen substituent (leaving group) this is known as **Nucleophilic Substitution Reaction**.

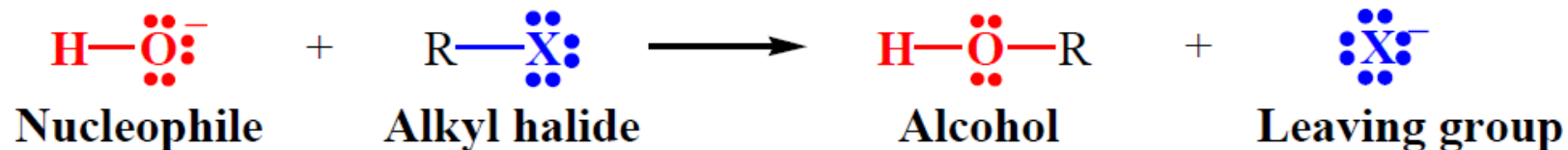


In Nucleophilic substitution reactions, the C-X bond of the substrate undergoes *heterolysis*, and the lone-pair electrons of the nucleophile is used to form a new bond to the carbon atom.

A nucleophile (“nucleus loving”, or “positive-charge loving”) is a reactant that provides a pair of electrons to form a new covalent bond.

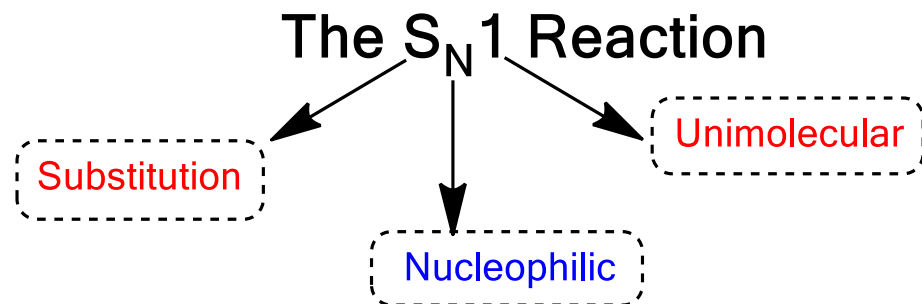
There are Two types of Nucleophilic substitution reactions called

- 1) **SN1 : Unimolecular Nucleophilic Substitution**
- 2) **SN2 : Bimolecular Nucleophilic Substitution**



# SN1 : Unimolecular Nucleophilic Substitution

The SN1 reaction – **SN** stands for **Nucleophilic substitution** and the "1" represents the rate determining step is **Unimolecular**.



## Rate of SN1 reaction:

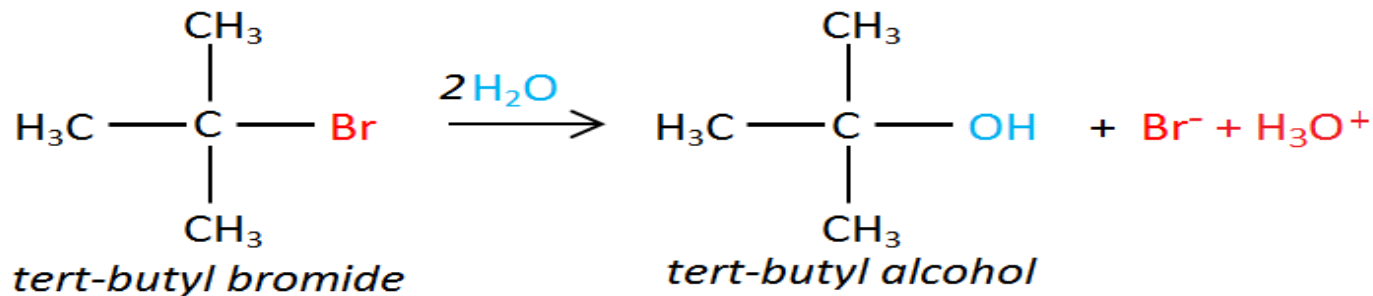
Rate of *SN1* reaction follow **first-order rate law** (1st order kinetics) .

According to the **kinetics of reactions**, their rate depends only on the **substrate's concentration [S]**.

$$\text{Reaction rate} \propto [S] / \text{Rate} = k[\text{RX}] \text{ only}$$

The order of reactivity of substrates for SN1 reactions is the reverse of SN2 -  $3^\circ > 2^\circ > 1^\circ$

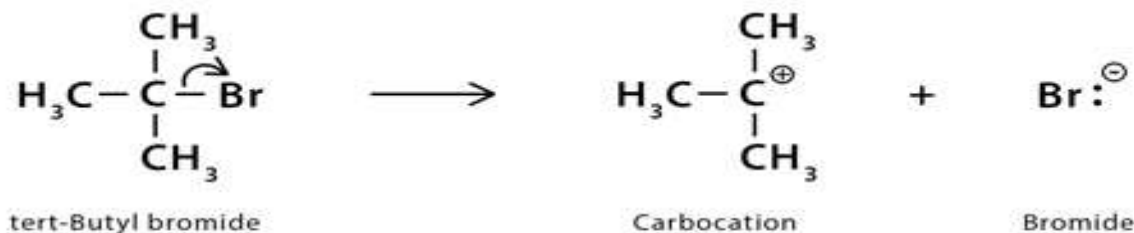
**Example: Hydrolysis of *tert*-butyl bromide to form *tert*-butyl alcohol.**



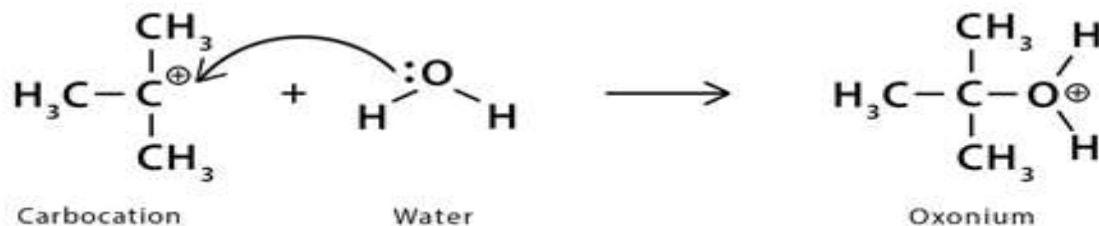
**Method-1:** The mechanism of SN1 reaction involves breaking the carbon-halogen bond to form a **carbocation intermediate**, followed by the addition of the nucleophile.

## Mechanism of SN1 Reaction

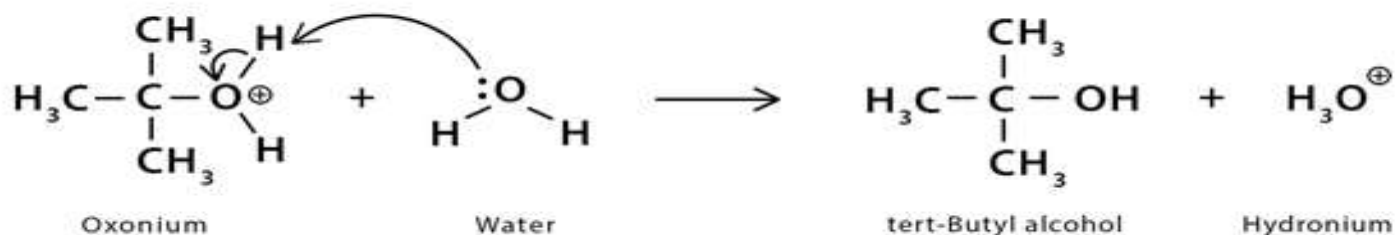
**Step 1:** Formation of a tert-butyl carbocation by separation of a bromide anion from the carbon atom of tert-butyl bromide.



**Step 2:** Nucleophilic attack of the carbocation by a water molecule, resulting in an oxonium ion intermediate.

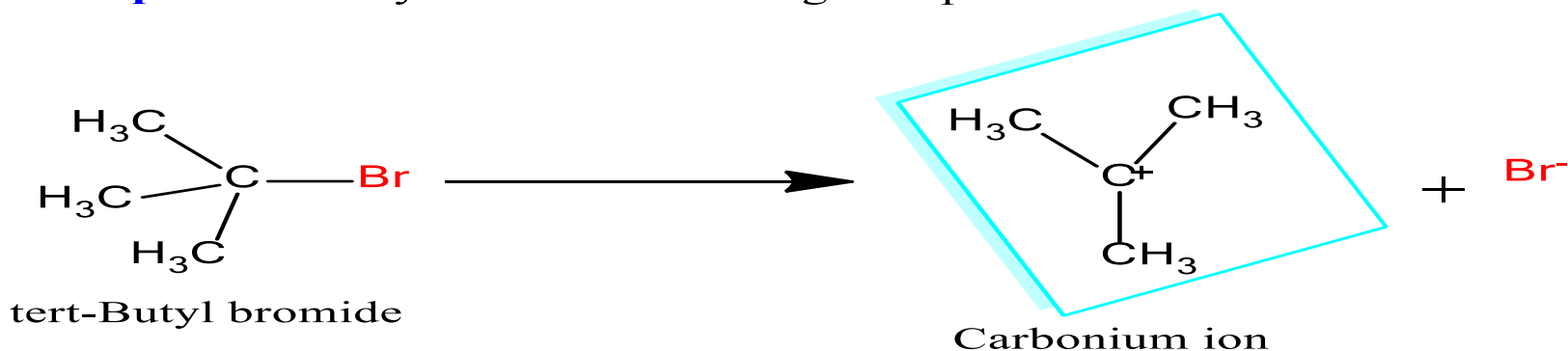


**Step 3:** Deprotonation of the protonated nucleophile by a second water molecule, which acts as a base, resulting in an alcohol and a hydronium ion.

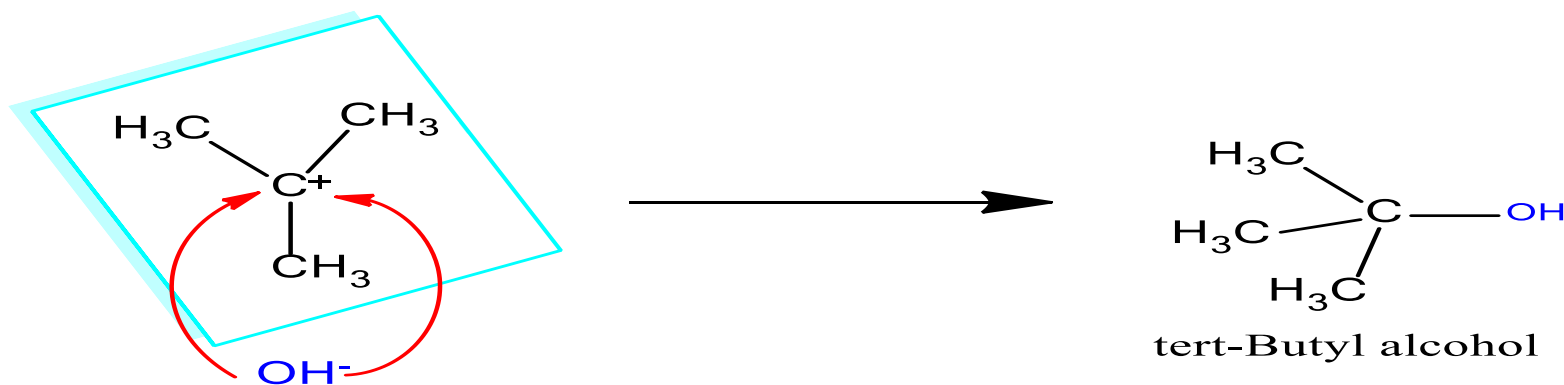


## Method-2: Easy way to understand SN1 Mechanism involves two steps

**Step-1:** The alkyl halide ionises to give a planar carbonium ion



**Step-2:** The nucleophile can attack the planar carbonium ion from either side to give the product.

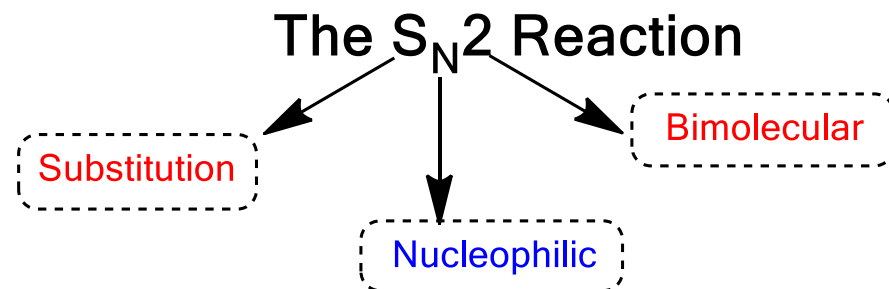


**Solvent Effect:** Polar protic solvents like H<sub>2</sub>O and ROH favor SN1 reactions because the ionic intermediates (both cations and anions) are stabilized by solvation.

**Stereochemistry:** SN1 mechanism forms a **racemic** mixture of two products. It is called as **Racemization**.

# SN2 : Bimolecular Nucleophilic Substitution

The SN1 reaction – **SN** stands for **Nucleophilic substitution** and the “2” represents the rate determining step is **Bimolecular**.



**Rate of SN2 reaction:**

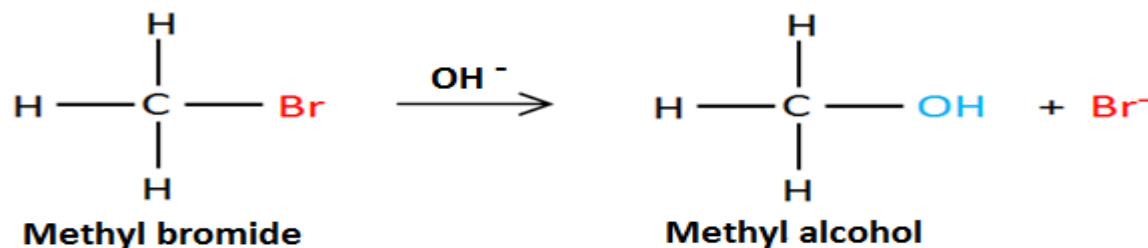
**Rate of SN2 reaction follow *second-order rate law* (2nd order kinetics) .**

Bimolecular means that the rate of an SN2 reaction is directly proportional to the concentration of two reacting molecules, the alkyl halide 'substrate (S)' and the nucleophile (Nu).

**Reaction rate  $\propto$  [Substrate] [Nucleophile] / Rate =  $k[\text{RX}] [\text{Nu}]$**

**The order of reactivity of substrates for SN2 reactions is the -  $1^\circ > 2^\circ > 3^\circ$**

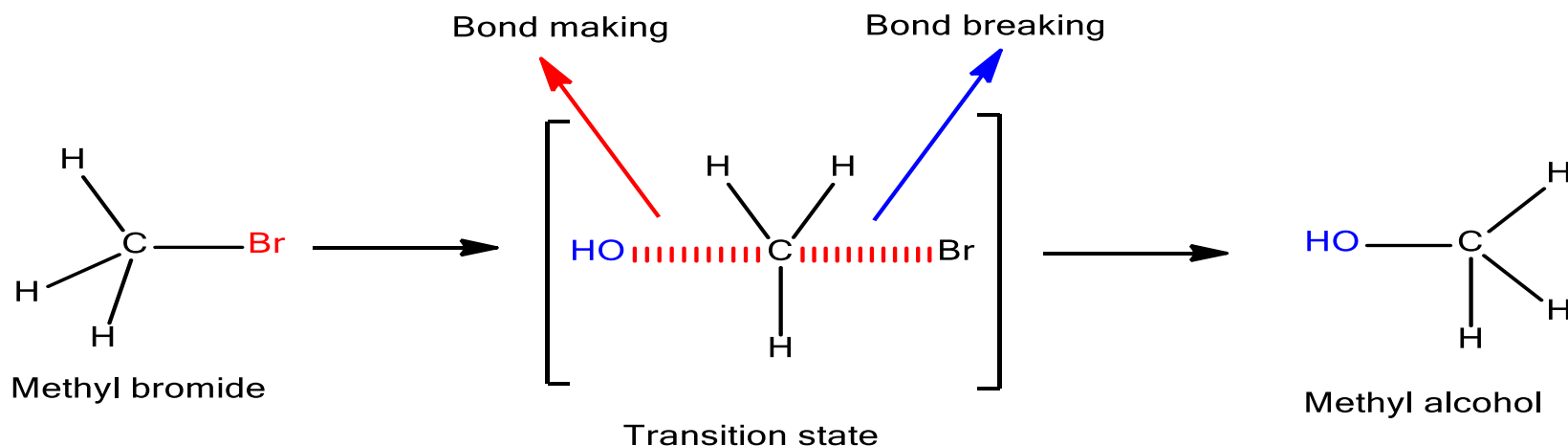
**Example: Hydrolysis of methyl bromide by aq. NaOH to form alcohol**



## Mechanism of SN2 Reaction:

The mechanism of SN2 reaction involves the simultaneous formation of the carbon-nucleophile bond and the breaking of the carbon-halogen bond.

**In an SN2 reaction, Nu-C bond formation and C-Leaving Group bond breakage happen simultaneously. In the transition state, the carbon is partially attached to both.**



**Stereochemistry:** SN2 mechanisms always proceed via rearward (back side) attack of the nucleophile on the substrate. This process results in the inversion of the relative configuration, going from starting material to product. **This inversion is often called the Walden inversion.**

**Solvent:** Polar aprotic solvent (without OH) favors SN2. examples of polar aprotic solvents are **acetone, dimethylsulfoxide, N,N'-dimethylformamide, etc.**

## Comparison between S<sub>N</sub>1 and S<sub>N</sub>2 reaction mechanism

S <sub>N</sub> 2 reaction mechanism	S <sub>N</sub> 1 reaction mechanism
<b>One step</b> mechanism	<b>Two step</b> mechanism
<b>Bimolecular</b> reaction	<b>Unimolecular</b> reaction
Product formation takes place by <b>TS</b> (Transition State)	Product formation takes place by <b>carbocation intermediate</b>
<b>No carbocation rearrangement</b>	<b>Carbocation rearrangement</b>
Reaction is favoured by <b>polar aprotic solvents</b>	Reaction is favoured by <b>polar protic solvents</b>
Given mainly by <b>methyl halides</b>	Given mainly by <b>tertiary alkyl halides</b>
Reactivity of RX; <b>CH<sub>3</sub>X &gt; 1° &gt; 2° &gt; 3°</b>	Reactivity of RX; <b>3° &gt; 2° &gt; 1° &gt; methyl</b>
Mechanism is favoured when <b>nucleophile is an anion</b>	Mechanism is favoured when <b>nucleophile is neutral</b>
Reaction velocity depends on the concentration of nucleophile. <i>i.e.</i> mechanism is favored by high concentration of nucleophile	Reaction velocity is independent of the concentration of nucleophile.
$  \begin{array}{c}  \text{H} \\    \\  \text{H} - \text{C} - \text{Br} \\    \\  \text{H} \\  \text{Methyl bromide}  \end{array}  \xrightarrow{\text{OH}^-}  \begin{array}{c}  \text{H} \\    \\  \text{H} - \text{C} - \text{OH} \\    \\  \text{H} \\  \text{Methyl alcohol}  \end{array}  + \text{Br}^-  $	$  \begin{array}{c}  \text{CH}_3 \\    \\  \text{H}_3\text{C} - \text{C} - \text{Br} \\    \\  \text{CH}_3 \\  \text{tert-butyl bromide}  \end{array}  \xrightarrow{2\text{H}_2\text{O}}  \begin{array}{c}  \text{CH}_3 \\    \\  \text{H}_3\text{C} - \text{C} - \text{OH} \\    \\  \text{CH}_3 \\  \text{tert-butyl alcohol}  \end{array}  + \text{Br}^- + \text{H}_3\text{O}^+  $
<b>Inversion of configuration</b>	<b>Racemisation</b> S.Seetaram, Visit at <a href="http://www.pharmawisdom.co.in">www.pharmawisdom.co.in</a>

## Comparison of S<sub>N</sub>1 and S<sub>N</sub>2

Points	S <sub>N</sub> 1	S <sub>N</sub> 2
<i>Steps</i>	Two steps	One step
<i>Molecularity</i>	Unimolecular, only substrate is involved in rate determining step	Bimolecular, both substrate and nucleophile are involved in the reaction
<i>Kinetics and rate</i>	First order	Second order
<i>Stereochemistry</i>	Racemisation or partial racemization favouring product with inverted configuration	Complete inversion
<i>Effect of substrate structure on rate</i>	Stability of carbocation: Tertiary > secondary > primary > methyl	Steric hindrance decreases the rate of reaction: Methyl > primary > secondary > tertiary
<i>Effect of solvents on rate</i>	Polar protic solvents like water favours S <sub>N</sub> 1.	Polar aprotic solvent (without OH) favours S <sub>N</sub> 2, like acetone, DMSO
<i>Nucleophilicity and concentration of nucleophiles</i>	Weak nucleophiles of low concentration too can make the reaction to occur	Strong nucleophiles of high concentration increases the rate
<i>Leaving group effect</i>	Weakly basic and highly polarizable group increase the rate	Weakly basic and highly polarizable group increases the rate.
<i>Reaction intermediate</i>	carbocation	None
<i>Competition Reaction</i>	E1 (Elimination Unimolecular) and rearrangement	E2 (Elimination Bimolecular)

# Factors affecting SN1 and SN2 reactions

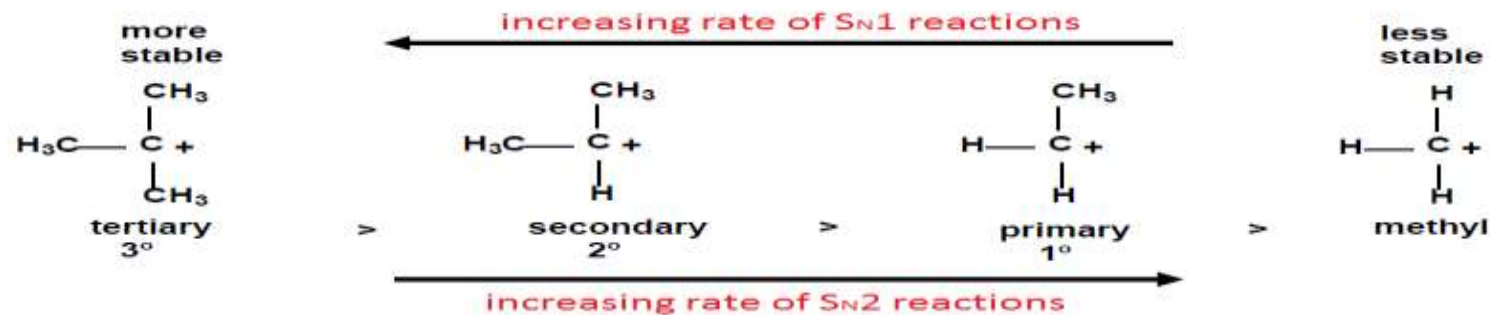
The rate of an SN1 & SN2 reaction depends upon 4 factors:

1. The nature of the substrate (the alkyl halide)
2. The power of the nucleophile
3. The ability of the leaving group to leave
4. The nature of the solvent

## Nature of the substrate (the alkyl halide):

In SN1 & SN2 reaction the substrate plays the most important part in determining the rate of the reaction. **Highly substituted alkyl halides (substrates) form a more stable Carbonium ion.** 3° alkyl halides undergo SN1 reactions with ease.

• Methyl and 1° alkyl halides undergo SN2 reactions with ease. • 2° Alkyl halides react more slowly. • 3° Alkyl halides do not undergo SN2 reactions. **Steric hindrance** caused by bulky R groups makes nucleophilic attack from the backside more difficult, slowing the reaction rate.



## Nature of the Nucleophile :

- A nucleophile with a negative charge is always more powerful than its conjugate acid.

Thus  $\text{OH}^-$  is more powerful than  $\text{H}_2\text{O}$  &  $\text{NH}_2^-$  is more powerful than  $\text{NH}_3$  &  $\text{CH}_3\text{O}^-$  is more powerful than  $\text{CH}_3\text{OH}$ , etc.

- The weak nucleophile favors an  $\text{SN1}$  mechanism
- The strong nucleophile favors an  $\text{SN2}$  mechanism

## Nature of the leaving group:

- The nature of the leaving group has the same effect on both  $\text{SN1}$  and  $\text{SN2}$  reactions.
- The better the leaving group, the faster a  $\text{C}^+$  can form and hence the faster will be the  $\text{SN1}$  reaction.
- The leaving group usually has a negative charge

**Example:** Iodine ( $-\text{I}$ ) is a good leaving group because iodide ( $\text{I}^-$ ) is non basic.

The hydroxyl group ( $-\text{OH}$ ) is a poor leaving group because hydroxide ( $\text{OH}^-$ ) is a strong base.

## The nature solvent :

There are 3 classes of organic solvents:

**Protic solvents:** which contain  $-\text{OH}$  or  $-\text{NH}_2$  groups.

**Polar aprotic solvents:** which contain strong dipoles but no  $-\text{OH}$  or  $-\text{NH}_2$  groups.

**Non polar solvents:** e.g., hydrocarbons.

**Polar protic solvents like H<sub>2</sub>O and ROH favor SN1 reactions** because the ionic intermediates (both cations and anions) are stabilized by solvation.

**Polar aprotic solvents favor SN2 reactions** because nucleophiles are not well solvated, and therefore, are more nucleophilic.

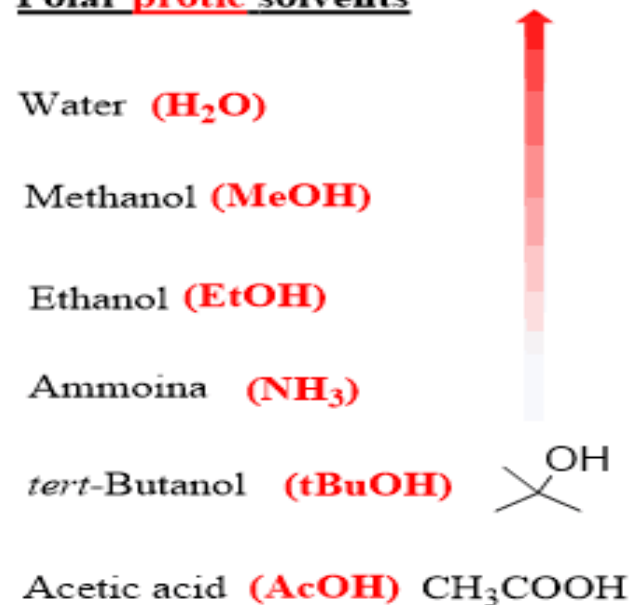
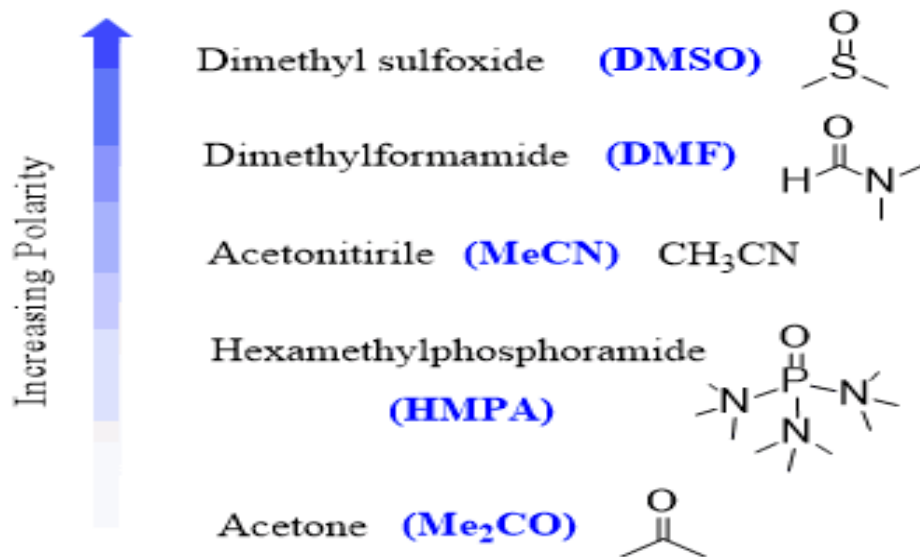
## Solvents

Polar aprotic solvents favor bimolecular S<sub>N</sub>2 and E2 mechanisms.

Polar protic solvents favor unimolecular S<sub>N</sub>1 and E1 mechanisms.

### Polar aprotic solvents

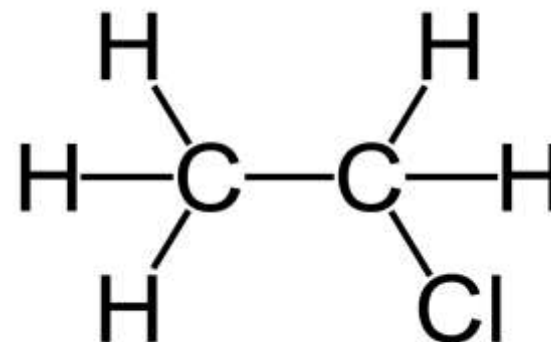
### Polar protic solvents



# Structure and Uses of Alkyl halides

## Ethylchloride:

**Chloroethane or monochloroethane**, commonly known by its old name Ethylchloride, is a chemical compound with chemical formula  $C_2H_5Cl$ , once widely used in producing tetraethyllead, a gasoline additive.



Chloroethane is produced by hydro chlorination of ethene:



## Uses:

- ✚ The major use of chloroethane was to produce **tetraethyllead (TEL)**, an **anti-knock additive for gasoline**.
- ✚ It is used in the **production of cellulose, dyes, medicinal drugs**, and other commercial products, and as a **solvent and refrigerant**.
- ✚ It is used as a mild **topical anesthetic** to numb the skin prior to ear piercing, skin biopsies, etc., and is also used in the treatment of sports injuries.
- ✚ Chloroethane is used to **convert cellulose to ethylcellulose, a thickening agent and binder in paints, cosmetics, and similar products**.

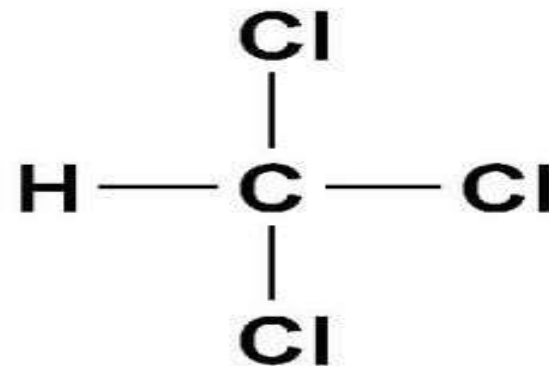
## Chloroform:

**Chloroform or trichloromethane** is an organic compound with formula  $\text{CHCl}_3$ .

It is a colorless, sweet-smelling, dense liquid.

It is a precursor to **PTFE (Polytetrafluoroethylene)**.

It is also a precursor to various **refrigerants**.



In industry, chloroform is produced by heating a mixture of **chlorine and methane**. At  $400 - 500^\circ\text{C}$ , a free radical halogenation occurs, yield chloroform

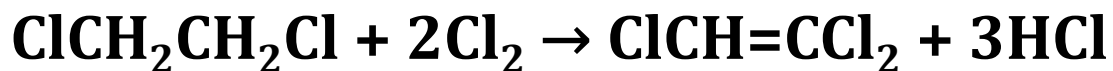
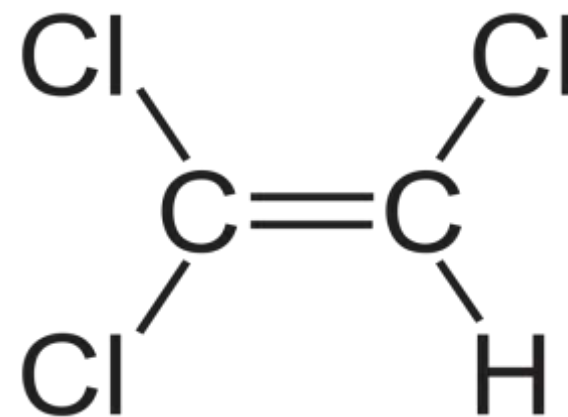
## Uses:

- ✚ It is used **as a solvent** for lacquers, floor polishes, resins, adhesives, alkaloids, fats, oils and rubber.
- ✚ **Chloroform** is used in making Fluorocarbon- 22, a refrigerant.
- ✚ Chloroform is also used to extract and **purify penicillin**.
- ✚ Chloroform used for **extraction and purification of Alkaloids**.
- ✚ Chloroform was popular as an **anesthetic** from the mid-1800s to around 1900, but it was found to cause death from paralysis. It also depresses most of the body's other organs, including the blood vessels, liver, pancreas, & kidneys. It is toxic to the liver and chloroform was replaced by safer compounds after about 1940.
- ✚ Chloroform gives relieve the pain of childbirth.

## Trichloroethylene:

It is a halocarbon commonly used as an industrial solvent. It is a clear non-flammable liquid with a sweet smell.

When 1, 2-dichloroethane heated with chlorine at 400°C is produced to trichloroethylene.

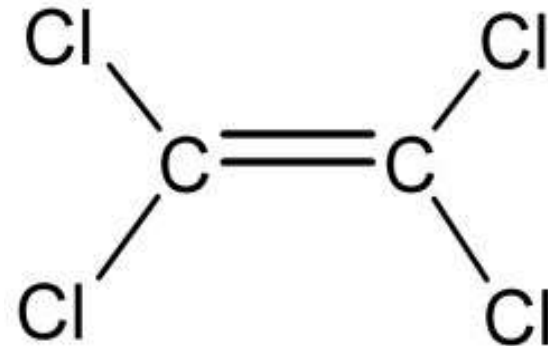


## Uses:

- ✚ The main use of trichloroethylene is in the **vapor degreasing of metal parts.**
- ✚ Trichloroethylene is also used as an **extraction solvent** for greases, oils, fats, waxes, and tars, a chemical intermediate in the production of other chemicals, and **as a refrigerant.**
- ✚ Trichloroethylene is used in consumer products such as typewriter correction fluids, paint removers/strippers, adhesives, spot removers, and rug-cleaning fluids.
- ✚ Trichloroethylene was used in the past as a **general anesthetic.**

## Tetrachloroethylene:

It is a volatile chlorinated organic hydrocarbon that is widely used as a **solvent** with the chemical formula  $C_2Cl_4$ . It is non-flammable liquid at room temperature, evaporates easily into the air and has a sharp sweet odour.



It is prepared by thermal decomposition of hexachloroethane.



### Uses:

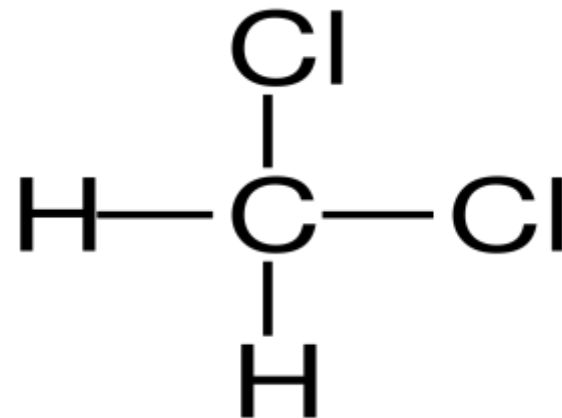
- + Tetrachloroethylene is an excellent solvent for organic materials.
- + It is widely used in dry cleaning.
- + It is also used to degrease metal parts in the automotive and other metalworking industries, usually as a mixture with other chlorocarbons.
- + It appears in a few consumer products including paint strippers and spot removers.
- + It is also used in aerosol preparations.

## Dichloromethane:

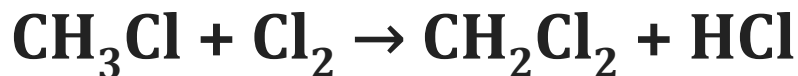
Dichloromethane (**DCM** or **methylene chloride**) is an organic compound with the formula  $\text{CH}_2\text{Cl}_2$ .

This colorless, volatile liquid with a moderately sweet aroma is widely used as a **solvent**.

Although it is not miscible with water, it is miscible with many organic solvents.



DCM is produced by treating chloromethane with chlorine gas at 400–500 °C.



## Uses:

- ✚ DCM is a useful **solvent** for many chemical processes.
- ✚ It is widely used as a **paint stripper and a degreaser**.
- ✚ In the food industry, it has been used to **decaffeinate coffee and tea** as well as to prepare extracts of hops and other flavorings.
- ✚ Used as a blowing agent for polyurethane foams.
- ✚ It is also used in shoe manufacturing.
- ✚ It is a solvent in paint removers, degreasing fluids, aerosol propellants and hair lacquers.

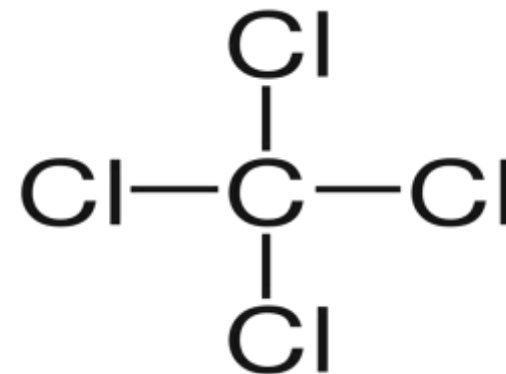
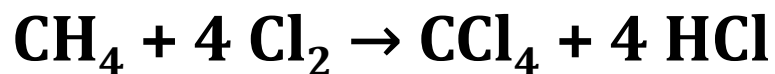
## Tetrachloromethane:

It is also known as **Carbon tetrachloride (CCl<sub>4</sub>)**.

It was formerly used in **fire extinguishers**, as a precursor to **refrigerants** and as a **cleaning agent**.

It is a colorless liquid with a "sweet" smell that can be detected at low levels.

It is mainly produced from methane:



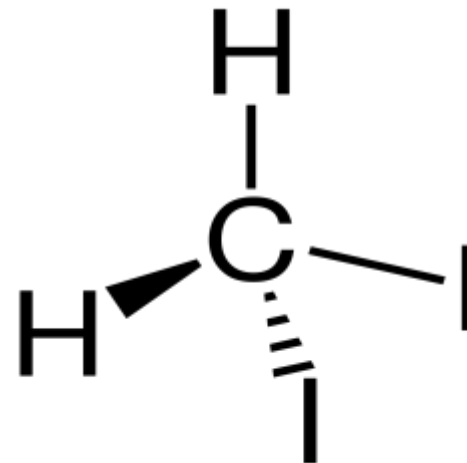
## Uses:

- ✚ Carbon tetrachloride was used to produce the chlorofluorocarbon refrigerants **R-11** (trichlorofluoromethane) & **R-12** (dichlorodifluoromethane).
- ✚ Carbon tetrachloride has also been used in the **detection of neutrinos**.
- ✚ It is a useful **solvent for halogenations**.
- ✚ Carbon tetrachloride was widely used as a **dry cleaning solvent**, and metal degreasing solvent.
- ✚ Carbon tetrachloride is one of the **most potent hepatotoxins** (toxic to the liver), so that it is widely used in scientific research to evaluate **Hepatoprotective agents**.
- ✚ It is also used as a starting material (building block) for making other chemicals and is used in some consumer products.

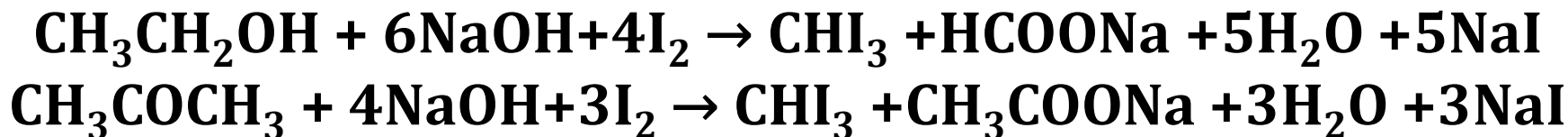
## Iodoform:

It is also known as tri-iodomethane, carbon triiodide, and methyl triiodide.

It is the organo iodine compound with the formula  $\text{CHI}_3$ . It is a pale yellow, crystalline, volatile substance, it has a penetrating and distinctive odor and, analogous to chloroform, sweetish taste.



Iodoform was prepared by ethanol or acetone with Iodine



## Uses:

- ✚ It is occasionally used as a **disinfectant**.
- ✚ It was used in medicine as a **healing and antiseptic** dressing for wounds and sores.
- ✚ It is the active ingredient in many ear powders for dogs and cats, along with zinc oxide and propanoic acid, which are used to prevent infection and facilitate removal of ear hair.

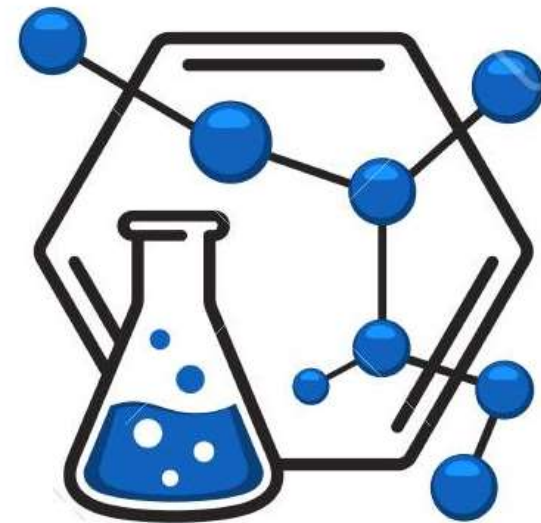
# ALCOHOLS

**B. Pharm. I Year II Sem.**

**(As per PCI)**

## Topics Covered:

- ▶ Quality Tests for Alcohols
- ▶ Structure & Uses of Alcohols



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# ALCOHOLS

The organic compound which has -OH functional group are called **alcohols**. The general formula for alcohol is  $C_nH_{2n+1}OH$  / **R-OH**.

## Classification of Alcohol:

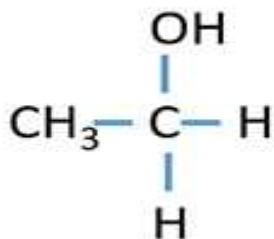
On the basis of -OH group attached to the carbon atom, alcohols are divided into three categories:

**Primary alcohol:** When the carbon atom attached to the hydroxyl group is bonded to only one carbon atom such type of alcohol is known as **primary alcohol**.

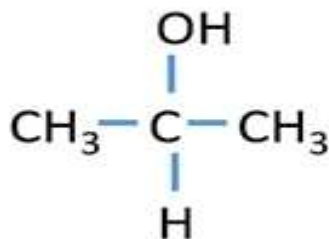
**Secondary alcohol:** When it is bonded to two carbon atoms such type of alcohol is known as **secondary alcohol**.

**Tertiary alcohol:** When it is bonded to three carbon atoms such type of alcohol is known as **tertiary alcohol**.

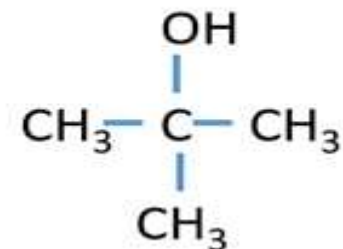
Primary alcohols



Secondary alcohols



Tertiary alcohols



## Types of Alcohol:

Depending on the number of hydroxyl groups attached, alcohols can be classified into three types.

**Monohydric alcohols:** They contain one -OH group. Example:  $\text{CH}_3\text{CH}_2\text{-OH}$

**Dihydric alcohols:** They contain two -OH groups. They are also called diols & Glycols.

Example: 1,2-Ethandiol.

**Trihydric alcohols:** They contain three -OH groups. They are also called Triols or glycerols.

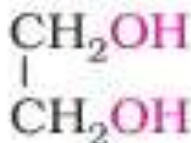
Example: 1,2,3-Propantriol.

**Polyhydric alcohols:** They contain more than three -OH groups.

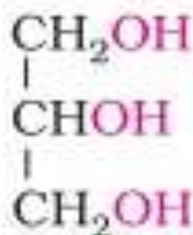
Example: sarbitol



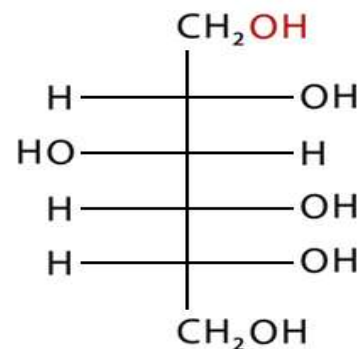
Monohydric



Dihydric



Trihydric



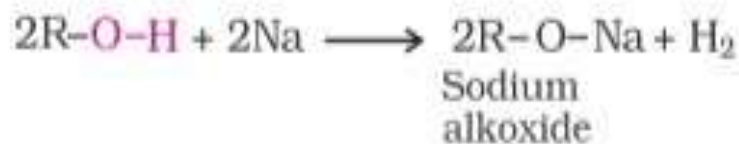
Sorbitol

## Physical Properties of Alcohol:

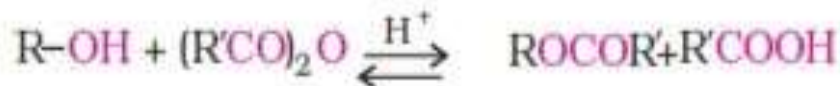
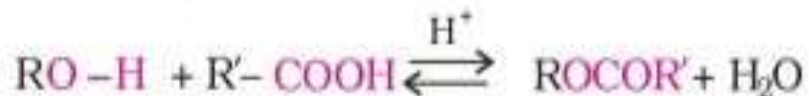
- The solubility of alcohol in water depends upon the length of alkyl chain in the alcohol
- They are weak acid.
- They have higher boiling point than alkane, alkene and alkyne

## Chemical Properties of Alcohol:

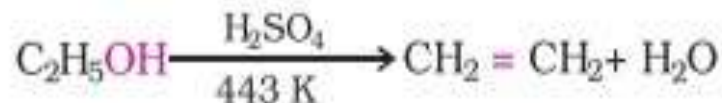
- On reacting with active metals such as sodium, potassium and aluminium they yield corresponding alkoxides/phenoxides and hydrogen.



- On reacting with carboxylic acids, acid chlorides and acid anhydrides they form esters



- On treating with protic acid e.g. concentrated  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$ , they undergo dehydration



## Qualitative tests for Alcohols

The following tests may be used to detect the presence of an **-OH group** in organic compounds.

For these tests, take the liquid compound or a solution of solid compound in an inert solvent such as dry ether or benzene.

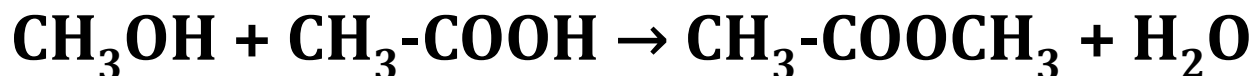
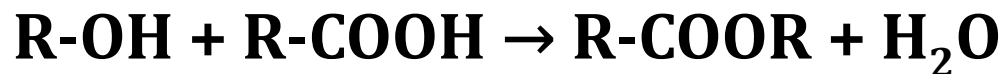
- A) Esterification Test :
- B) Sodium metal test
- C) Phosphorus Pentachloride Test
- D) Ceric ammonium nitrate test
- E) Acetyl chloride test

### A) Esterification Test:

Carboxylic acid reacts with alcohols forming a fruit smelling ester. The reaction between an alcohol and a carboxylic acid is called ***Esterification***.

This reaction is a slow reaction catalysed by concentrated sulfuric acid.

The chemical reaction is given below.

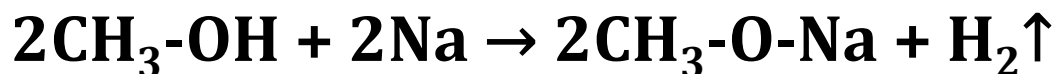
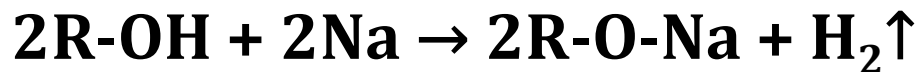


**Note:** A sweet smell indicates the presence of alcoholic group.

## B) Sodium Metal Test:

It is based on the *appearance of brisk effervescence* due to the *liberation of hydrogen gas* when alcohol reacts with active metals like sodium.

The chemical reaction is given below.



**The alcohol to be tested should be dry because water also reacts with sodium.** Sodium should be handled carefully, unreacted sodium should be destroyed by adding excess alcohol. This test is favorable if phenyl or carboxyl groups are absent.

*Note: Evolution of hydrogen gas cause a brisk effervescence indicates an alcoholic group.*

## C) Phosphorus Pentachloride Test:

Alcohol reacts with  $\text{PCl}_5$  results in the mixture becomes warm with evolution of HCl Gas, the given compound contains an -OH group.

The chemical equation is given below.



*Note: Evolution of HCl gas indicates an alcoholic group.*

## D) Ceric Ammonium Nitrate Test:

Alcohol or reaction with Ceric ammonium nitrate forms a pink or red colour precipitate due to the formation of a complex compound and ammonium nitrate. The chemical reaction is given below.



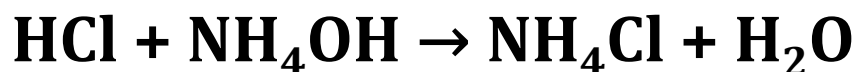
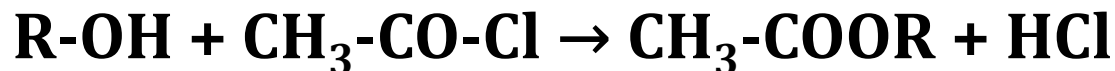
*Note: The appearance of red colour precipitate shows the presence of alcoholic group.*

## E) Acetyl Chloride Test:

Alcohol reacts with acetyl chloride results in the formation of ester and hydrogen chloride.

The resulting hydrogen chloride on contact with ammonium hydroxide forms a white fumes of ammonium chloride and water.

The chemical equation is given below.



*Note: The formation of white fumes indicates the presence of alcohol.*

## Distinction between Primary, Secondary and Tertiary Alcohols:

### 1) Lucas Test: (Lucas reagent - $\text{ZnCl}_2 + \text{Conc. HCl}$ )

The mixture of zinc chloride and concentrated hydrochloric acid is called Lucas reagent.

It reacts with primary, secondary and tertiary alcohols at different rates. This reagent forms a cloudiness on reacting with alcohols.

*Tertiary alcohols reacts immediately and give cloudiness, secondary alcohols reacts slowly and gives cloudiness after 5 to 10 minutes and there is no reaction with primary alcohols, this because primary alcohols do not react with Lucas Reagent at room temp. High temperatures are needed.*

#### Lucas test



Cloudiness appears only on heating or clear solution  
-> Primary alcohols



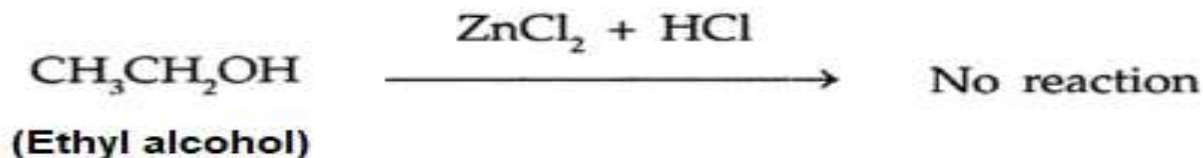
Cloudiness appears within five to ten minutes  
-> Secondary alcohols



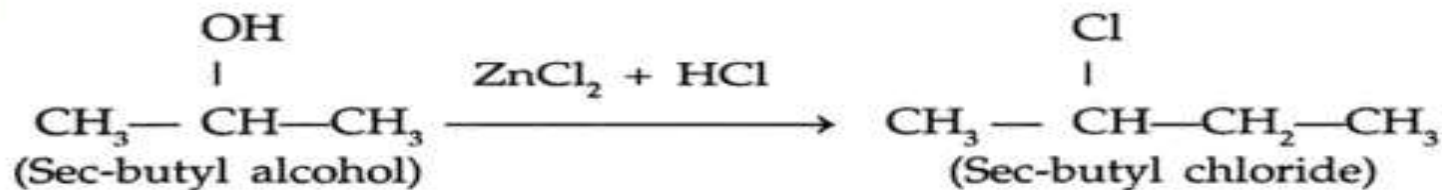
Cloudiness appears immediately  
-> Tertiary alcohols

## The chemical reactions are given below.

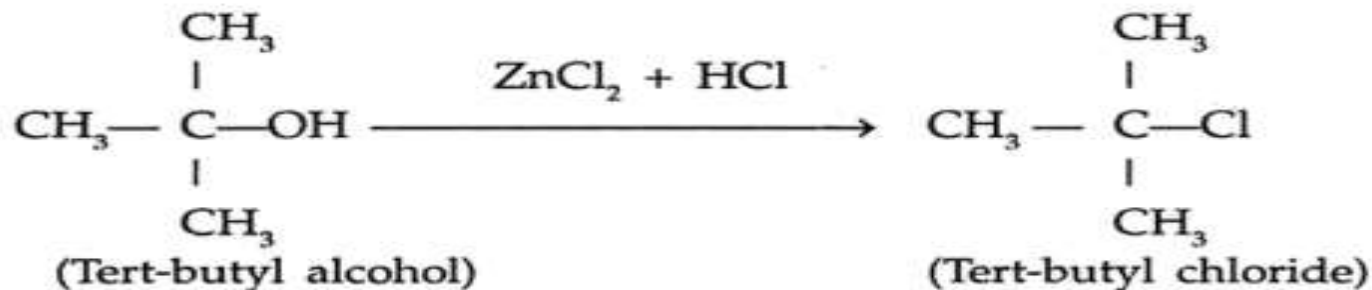
(i)



(ii)



(iii)



### **Note:**

*Cloudiness appears immediately → Tertiary alcohols*

*Cloudiness appears within five to ten minutes → Secondary alcohols*

*Cloudiness appears only on heating → Primary alcohols*

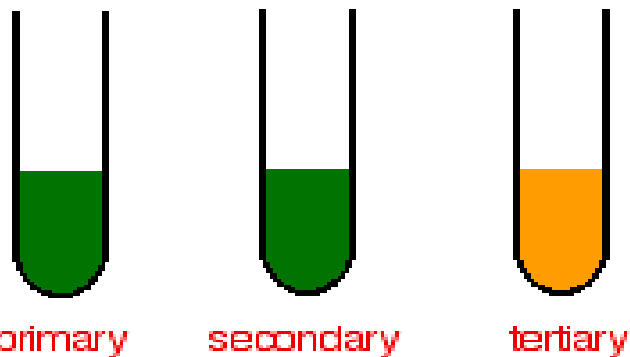
## 2) Oxidation Test (Dichromate Test)

In the oxidation test, the alcohols are treated with **sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7$ ) in sulphuric Acid (orange solution)**. The rate of oxidation varies between primary, secondary and tertiary alcohol. On the basis of their oxidation rates, alcohols can be distinguished as:

**Primary alcohol** gets easily oxidized to an aldehyde and can further be oxidized to carboxylic acids too. **There will be a change in colour of the solution from orange to green.**

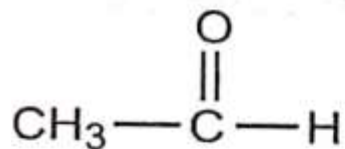
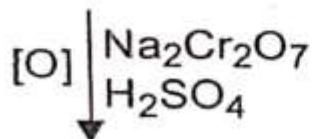
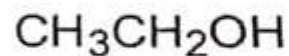
**Secondary alcohol** gets easily oxidized to ketone but further oxidation is not possible. **There will be a change in colour of the solution from orange to green.**

**Tertiary alcohol** doesn't get oxidized in the presence of sodium dichromate. **Solution will remain orange.**

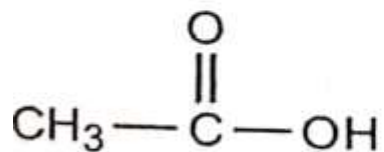


## DICHROMATE TEST

*Primary alcohol*



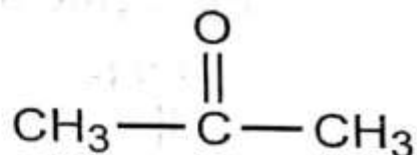
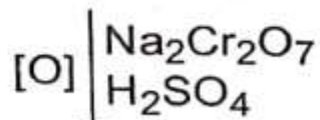
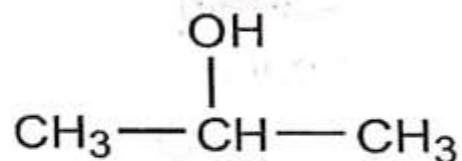
Aldehyde



Acid

(orange solution becomes green)

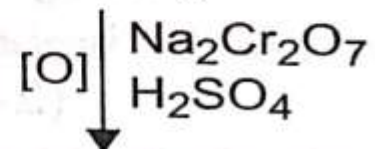
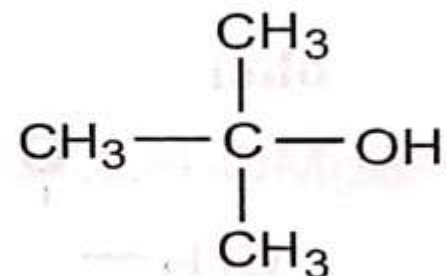
*Secondary alcohol*



Ketone

(orange solution becomes green)

*Tertiary alcohol*



No reaction  
(solution remains orange)

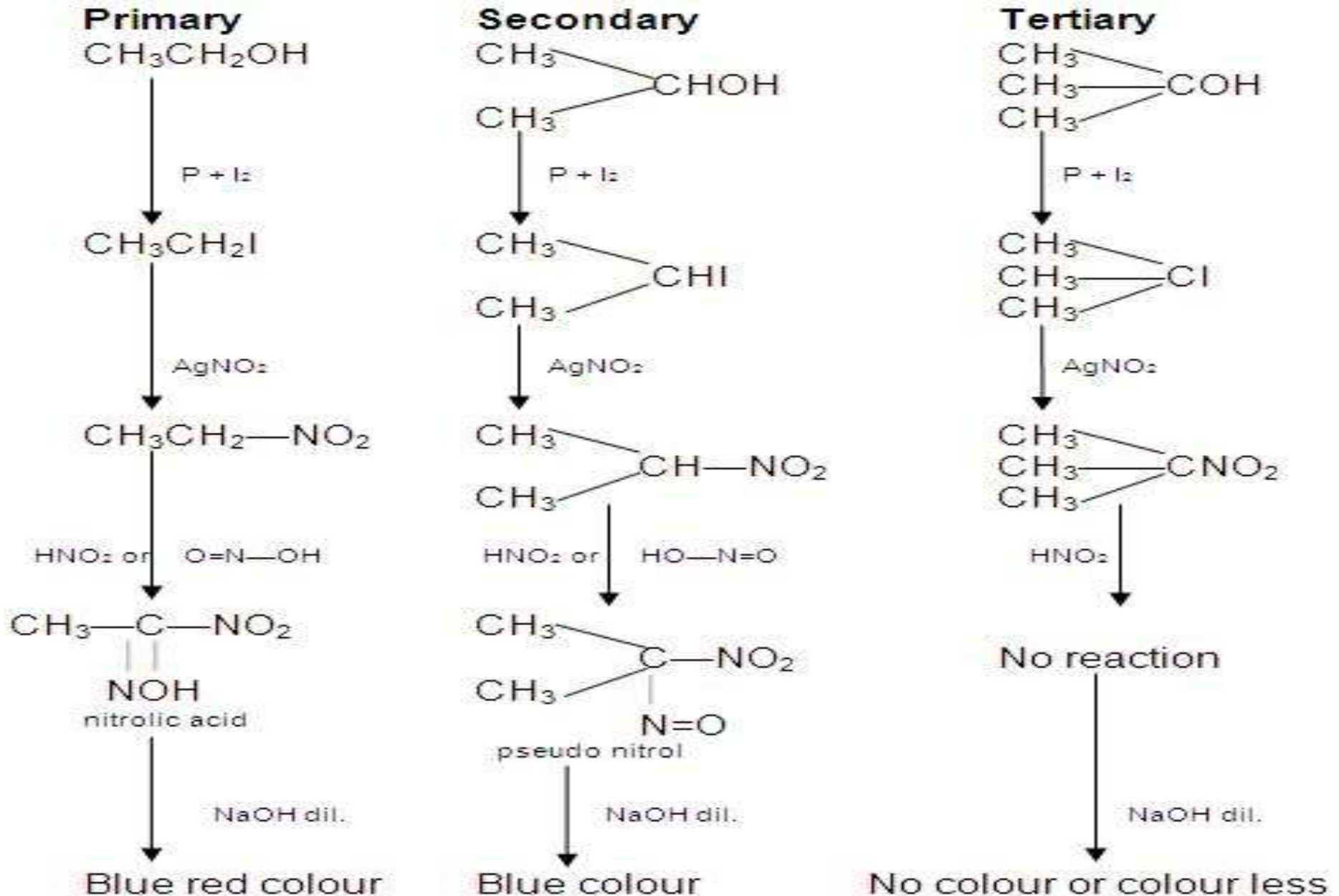
### 3) Victor Meyer test:

Victor Mayer method is one of the most important methods of identification of alcohols. In this methods primary, secondary and tertiary alcohols are subjected to a series of chemical analysis and the colour of resulting solution is observed.

**The different steps involved in Victor Meyer methods are as below :**

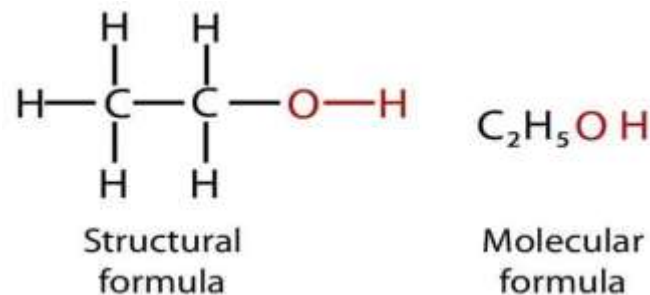
1. The **alcohol** is treated with **iodine** in presence of **red phosphorous** to obtain **Iodoalkane**.
2. Iodoalkane so formed is allowed to react with **alcoholic silver nitrate** in order to obtained **nitroalkane**.
3. The nitroalkane is treated with **nitrous acid (the mixture of  $\text{NaNO}_2 + \text{HCl}$ )** and the resulting solution is made alkaline.
4. **The colour of resulting solution is observed in which following observations are observed.**
  - a. **A primary alcohol gives blood red colour.**
  - b. **A secondary alcohol gives the blue colour.**
  - c. **A tertiary alcohol does not produce any colour.**

# Following reactions are involved in the Victor Meyer methods.



## Ethyl alcohol:

It is also known as alcohol, Ethanol and drinking alcohol, is a chemical compound, a simple alcohol with the chemical formula  $C_2H_5OH$  or  $CH_3-CH_2-OH$ .



Ethanol in alcoholic beverages and fuel is produced by fermentation. Certain species of yeast metabolize sugar, producing ethanol and carbon dioxide.



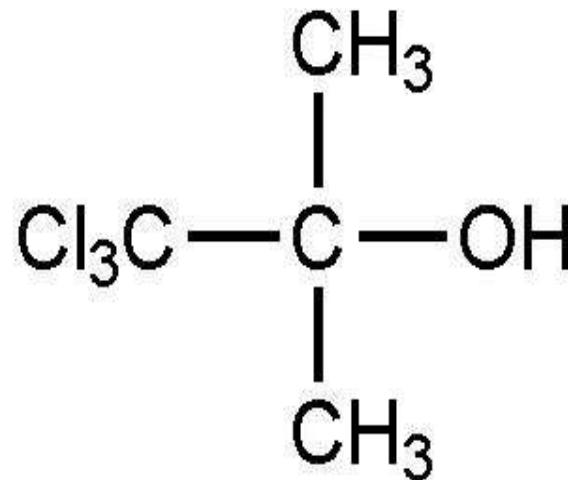
## Uses:

- ✚ Ethanol is used in medical wipes and most common antibacterial hand sanitizer gels **as an antiseptic**. Ethanol kills organisms by denaturing their proteins and is effective against most bacteria, fungi, and many viruses.
- ✚ Ethanol may be administered as **an antidote to methanol and ethylene glycol poisoning**.
- ✚ Ethyl Alcohol **increases the secretion of acids** in the stomach.
- ✚ Ethanol used as a **central nervous system depressant**. It can lift mood, cause feelings of euphoria, decrease anxiety.
- ✚ The largest single use of ethanol is as an **engine fuel and fuel additive**.
- ✚ Ethanol is miscible with water and is a good general purpose **solvent**. It is found in paints, tinctures, markers, and personal care products such **as mouthwashes, perfumes and deodorants**.

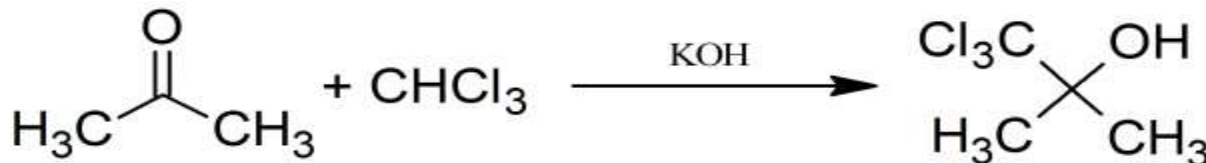
## Chlorobutanol:

Chlorobutanol (**trichloro-2-methyl-2-propanol**), is commonly used as a chemical preservative in a wide range of cosmetic and pharmaceutical products.

**The antibacterial and antifungal** properties of the substance inhibit microbial growth for extended periods of time.



Chlorobutanol is formed by the simple **Nucleophilic addition** of **chloroform** and **acetone** in presence of KOH / NaOH.



## Uses:

- ✚ Topically along with clove oil as **dental analgesic**.
- ✚ Chlorobutanol has been employed as **sedative and hypnotic**.
- ✚ Chlorobutanol used as **pharmaceutical aid** (antimicrobial) **antiseptic and local anesthetic**.
- ✚ It is used at a concentration of 0,5% as a **preservative** in injections, eye drops and mouth washes, salves, creams and ointments as well as cosmetics.

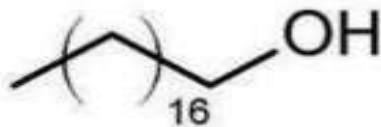
## Cetostearyl alcohol:

It is also known as **cetearyl alcohol** or **cetylstearyl alcohol** is a mixture of fatty alcohols, consisting predominantly of CETYL and STEARYL ALCOHOLS and is classified as a **fatty alcohol**.

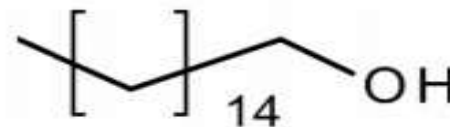


$n = \sim 14-16$

*Cetostearyl alcohol*



*Stearyl alcohols*



*Cetyl alcohol*

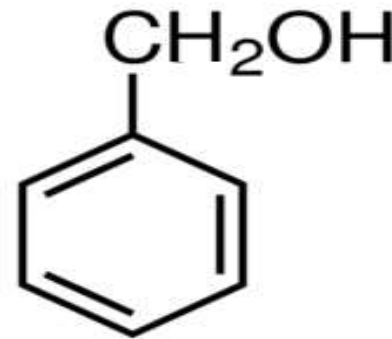
## Uses:

- ✚ Used in the cosmetic industry as an **opacifier** in shampoos, or as an **emollient, emulsifier or thickening agent** in the manufacture of skin creams and lotions.
- ✚ It is also employed as a **lubricant** for nuts and bolts, and is the active ingredient in some "liquid pool covers".
- ✚ It is used as an **emulsion stabilizer, opacifying agent, and foam boosting** surfactant, as well as an **aqueous and nonaqueous** viscosity-increasing agent.
- ✚ It imparts an emollient feel to the skin and can be used in **water-in-oil** emulsions, **oil-in-water** emulsions, and anhydrous formulations.

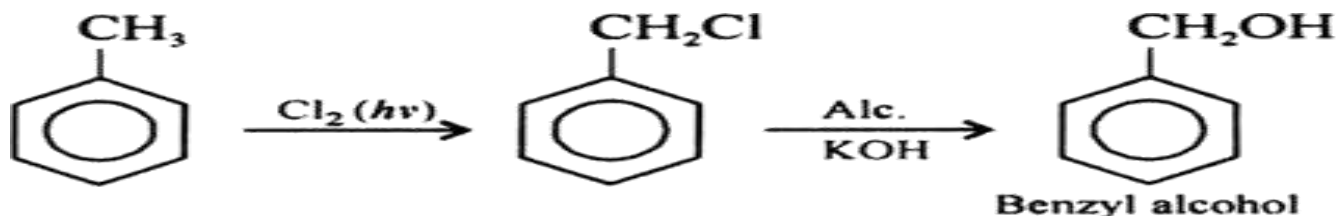
## Benzyl alcohol:

**Benzyl alcohol** is an aromatic **alcohol** with the formula  $C_6H_5CH_2OH$ . **Benzyl alcohol** is denoted as BnOH.

**Benzyl alcohol** is a colorless liquid with a mild pleasant aromatic odor.



Benzyl alcohol is prepared by the hydrolysis of benzyl chloride using KOH / NaOH:



## Uses:

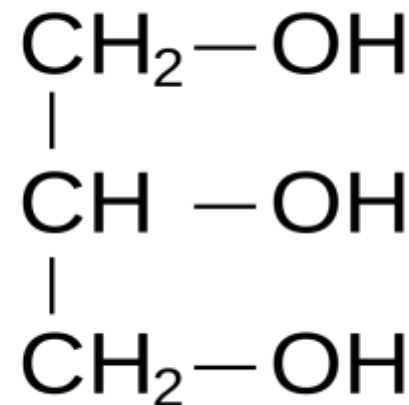
- ✚ Benzyl alcohol is used as a **general solvent** for inks, waxes, shellacs, paints, lacquers, and epoxy resin coatings.
- ✚ It is also used in **e-liquid for e-cigarettes** to enhance the flavors used.
- ✚ The use of benzyl alcohol as a 5% solution has been approved by the U.S. FDA for the treatment of head lice in children older than six months and in adults.
- ✚ As a **dye solvent**, it enhances the process of dyeing wool, nylon, and leather. - It also has use as a photographic developer, and as an insect repellent.
- ✚ Benzyl alcohol is used as a **bacteriostatic preservative** at low concentration in intravenous medications, **cosmetics**, and topical **drugs**.

## Glycerol:

It is also called **glycerine or glycerin**.

It is a simple **polyol** compound.

It is a colorless, odorless, viscous liquid that is sweet-tasting and non-toxic. The **glycerol** backbone is found in those lipids known as **glycerides**.



Glycerol is generally obtained from plant and animal sources where it occurs in triglycerides, esters of glycerol with long-chain carboxylic acids. The hydrolysis, saponification of these triglycerides produces glycerol.

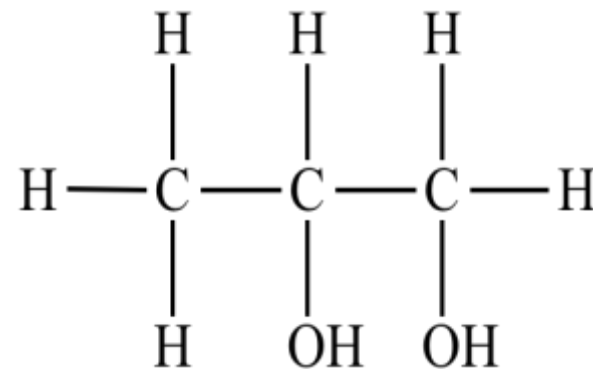
## Uses:

- ✚ Glycerol having **antimicrobial and antiviral properties** it is widely used in FDA approved **wound and burn treatments**.
- ✚ It can also be used as an effective marker to measure liver disease.
- ✚ It is also widely used as a **sweetener** in the food industry
- ✚ Glycerol is a component of glycerin soap.
- ✚ Glycerol is used in medical, pharmaceutical and personal care preparations, often as a means of improving smoothness, providing lubrication, and as a **humectant**.

## Propylene glycol:

Propylene glycol (propane-1,2-diol) is an organic compound with the chemical formula  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}$ .

It is a viscous, colorless liquid, which is nearly odorless but possesses a faintly sweet taste. Containing two alcohol groups, it is classed as a diol.



## Uses:

- ✚ Propylene glycol is a synthetic liquid substance that absorbs water.
- ✚ Propylene glycol is also used to **make polyester compounds**, and as a base for deicing solutions.
- ✚ Propylene glycol is used by the chemical, food, and pharmaceutical industries as **antifreeze** when leakage might lead to contact with food.
- ✚ Propylene glycol is also used in various **edible items** such as coffee-based drinks, liquid sweeteners, ice cream, whipped dairy products and soda.
- ✚ Propylene glycol is used **as a solvent** in many **pharmaceuticals, including oral, injectable, and topical formulations.**



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