Hydroxy Compounds

II B.Sc.

Semester - III

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Outlines

- Introduction
- Nomenclature
- Classification
- Preparation
- Physical Properties
- Chemical Properties
- Summary

Introduction

- Organic compound containing a hydroxyl (OH) functional group is called as alcohol.

  R – OH, where R is alkyl or substituted alkyl

- Compounds that have OH group directly attached to benzene ring is called as Phenols.

  Aryl – OH, where Aryl is phenyl or substituted phenyl

- These are used in making of cosmetics, fuel and alcoholic beverages also used as fuels and solvents.

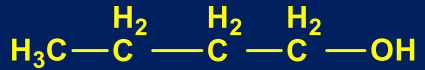
Nomenclature

- **IUPAC Nomenclature:**

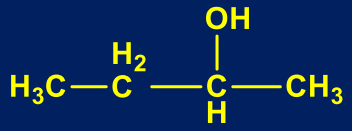
Step-1: select the longest continuous chain of carbon atoms containing hydroxyl group; it determines the root name and – "**ol**" is used as suffix.

Step-2: Identify substituents and assign the numbering to the parent chain to get hydroxyl group the lowest possible number.

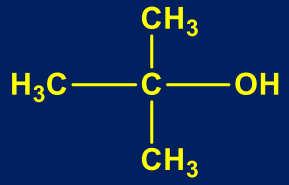
Examples:



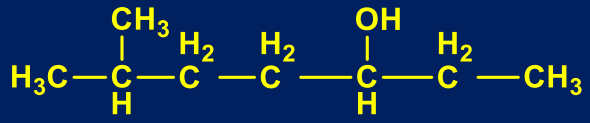
Butan-1-ol



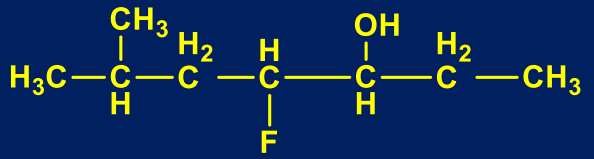
Butan-2-ol



2-methylpropan-2-ol



6-Methyl-3-heptanol



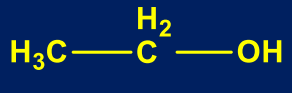
4-Fluoro-6-methyl-3-heptanol

❑ Common Nomenclature:

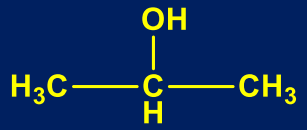
Common names are often used for simple alcohols

Rules to assign:

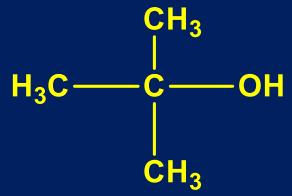
- Name all the carbon atoms of the given molecule as a single alkyl group.
- Name of the alkyl group followed by word alcohol



Ethyl alcohol



Isopropyl alcohol



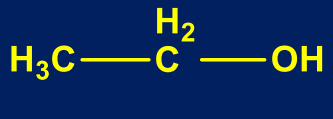
Tertiary butyl alcohol

Classification

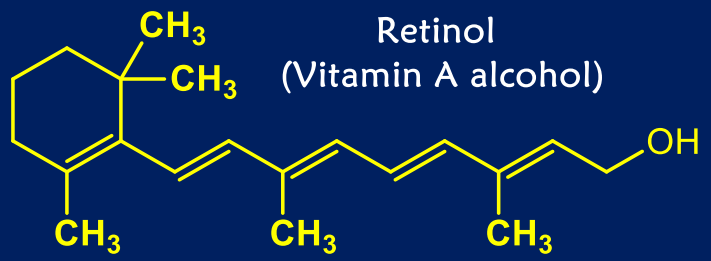
- According to type of carbon atom attached to –OH group mono hydric alcohols are classified into Primary (1°), Secondary (2°) and Tertiary (3°).

1. **Primary alcohol:** OH group is attached to primary carbon atom. General formula is RCH_2-OH

Ex:



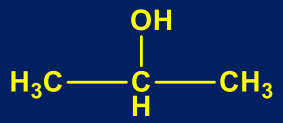
Ethanol



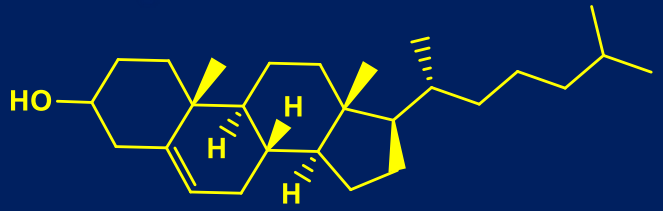
Retinol
(Vitamin A alcohol)

2. Secondary alcohol: OH group is attached to secondary carbon atom. General formula is $R_2CH\text{-}OH$

Ex:



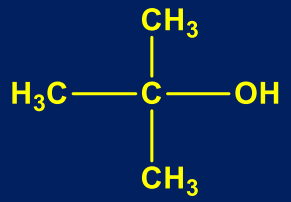
2-Propanol



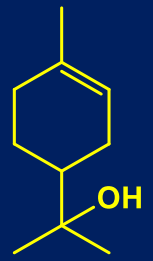
Cholesterol

3. Tertiary alcohol: OH group is attached to tertiary carbon atom. General formula is $R_3CH\text{-}OH$

Ex:



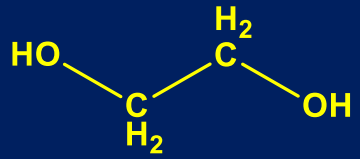
Tertiary butanol



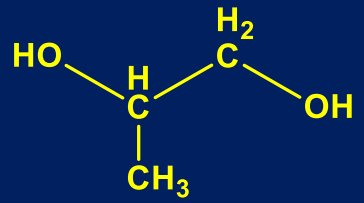
α -Terpineol

- **Polyhydric alcohols:** Alcohols that contains more than one OH group attached to different carbon atoms are called polyhydroxy alcohols.

- Dihydroxy ---------a compound contains two -OH groups



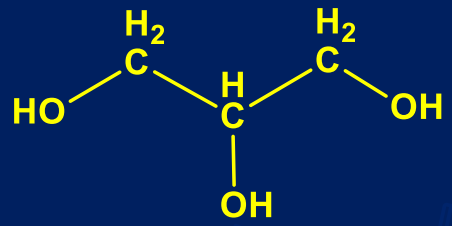
Ethylene glycol



Propane-1,2-diol

- Trihydroxy --------a compound contains three -OH groups

Glycerol

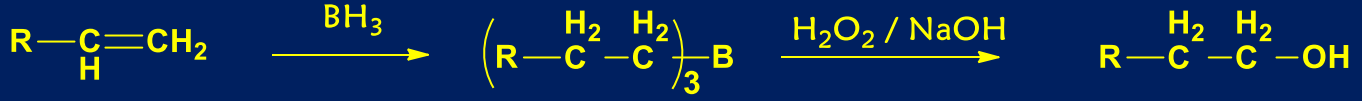


Preparation methods

1. Hydroboration – Oxidation:

- This reaction is used to convert alkenes to alcohols.
- It is a two-step reaction process; in that first step is conversion of alkene into trialkylboranes again this was converted to alcohol in the second step.
- Net reaction is an anti-Markovnikov addition of water across the double bond.

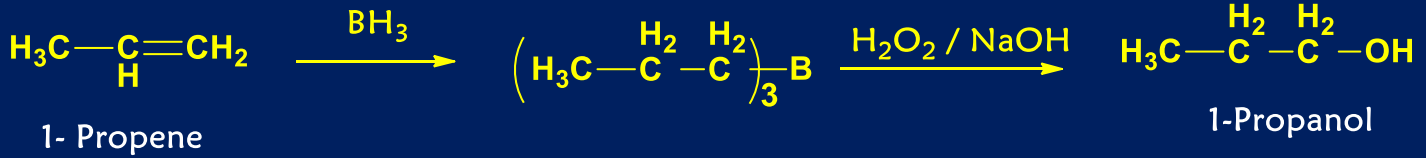
General equation:



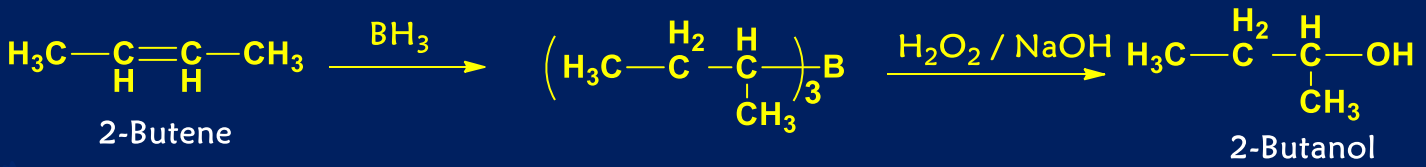
Alkene — Trialkyl Boranes — Alcohol

Ex:

- 1-Propene is converted to 1-propanol



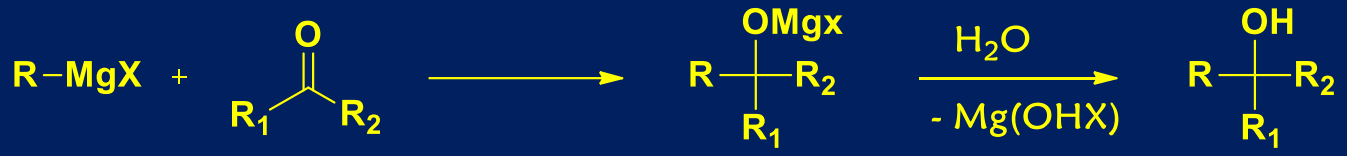
- 2-butene is converted to 2-butanol



2. From Grignard reagent:

- carbonyl compounds (aldehyde or Ketone) reacts with Grignard reagent to form an organometallic intermediate, which is further converted to alcohol upon hydrolysis with water.

General Reaction:



Grignard Reagent

Carbonyl compopund

Organo metalllic intermediate

Alcohol

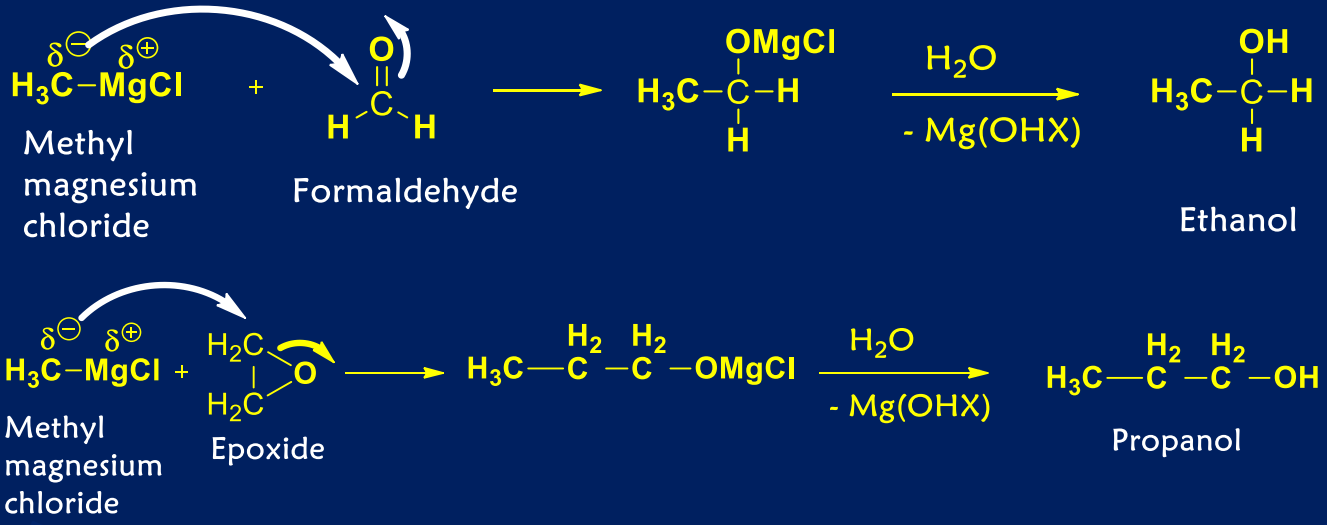
R = Alkyl

R_1, R_2 = H, Alkyl

X = Cl, Br and I

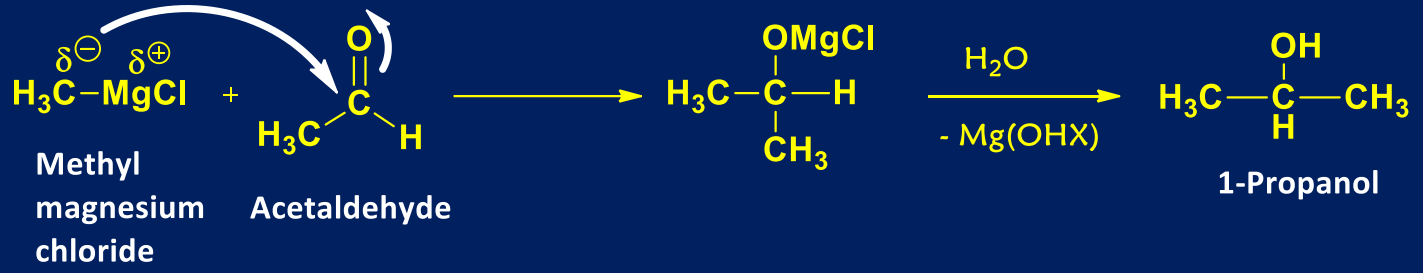
- By using this method we can easily prepare primary, secondary and tertiary alcohols.

Primary alcohol: Primary alcohols are formed when Grignard reagent is reacts with formaldehyde and Epoxide.



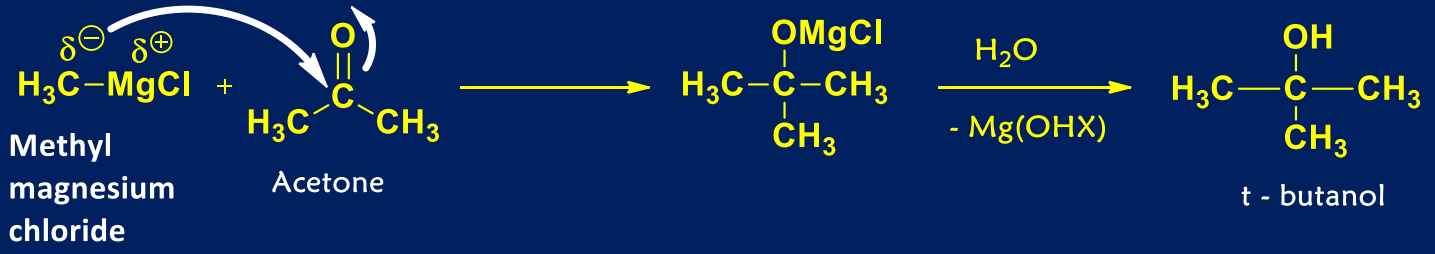
Secondary alcohol: Aldehydes (other than formaldehyde) reacts with Grignard reagent to form Secondary alcohols.

Ex: Acetaldehyde is converted to 2-propanol with methyl Grignard



Tertiary alcohol: Ketones reacts with Grignard reagent to form tertiary alcohols.

Ex: Acetone is converted to t-butanol with methyl Grignard.

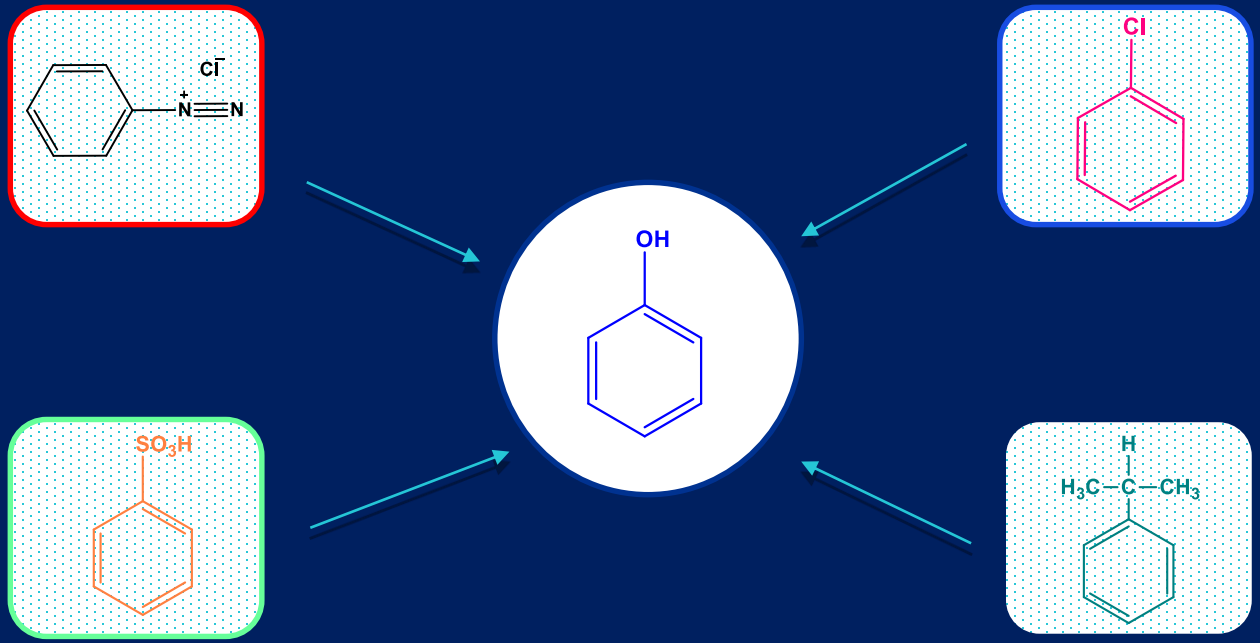


Methyl magnesium chloride

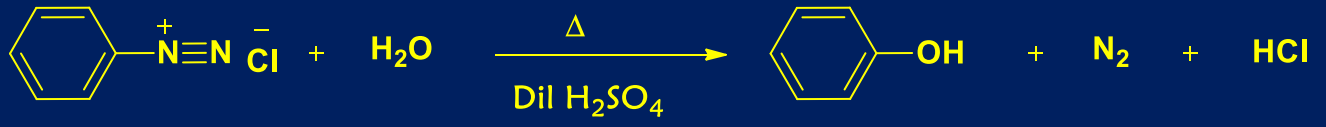
Acetone

t - butanol

Preparation of Phenol



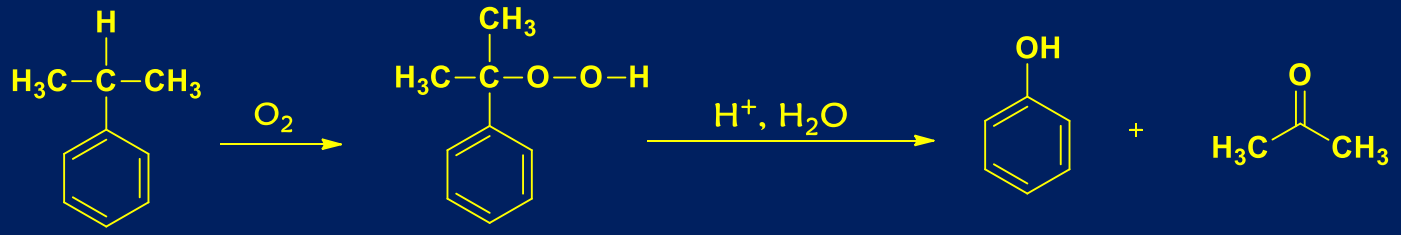
1. **From diazonium salts:** warming of an aqueous solution of benzene diazonium chloride undergoes hydrolysis to give phenol.



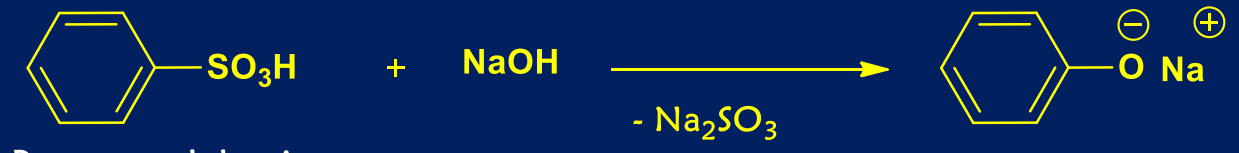
Benzene diazonium chloride

Phenol

2. From Cumene: on air oxidation, cumene forms cumene hydro peroxide which on further hydrolyzed in presence of dil. H_2SO_4 gives phenol.

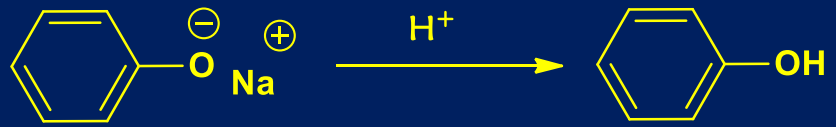


3. From Aryl Sulphonates: sodium phenate is formed by the fusion of sodium hydroxide with the sodium salt of benzene sulphonic acid, which is further converted to phenol in the presence of dil. acids.



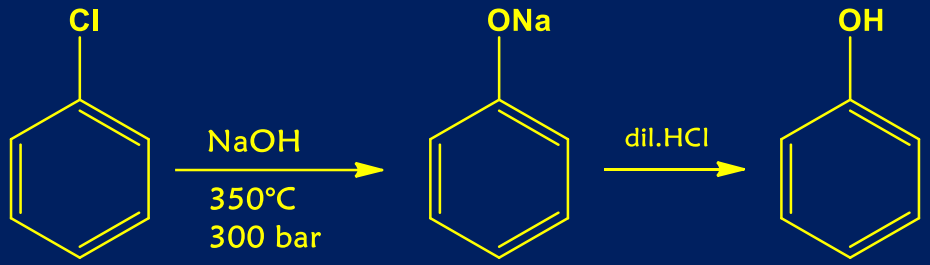
Benzene sulphonic Acid

Sodium Phenate



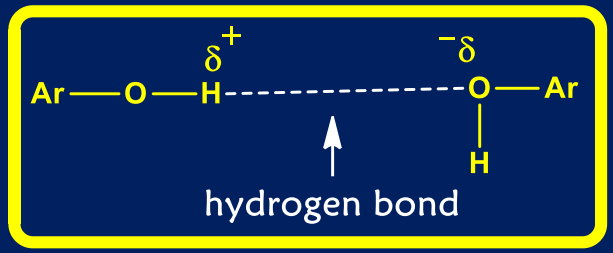
Phenol

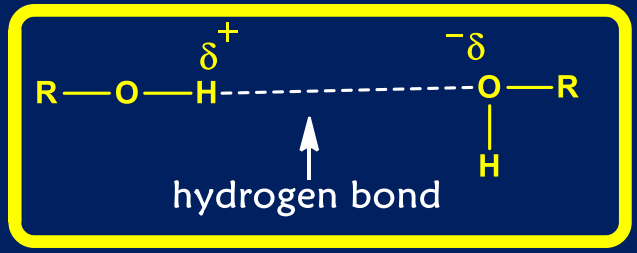
4. **Dow process:** In this process chloro benzene is treated with aqueous NaOH at 350°C and 300 atm pressure to form sodium phenoxide which is further acidified with acid to form phenol.



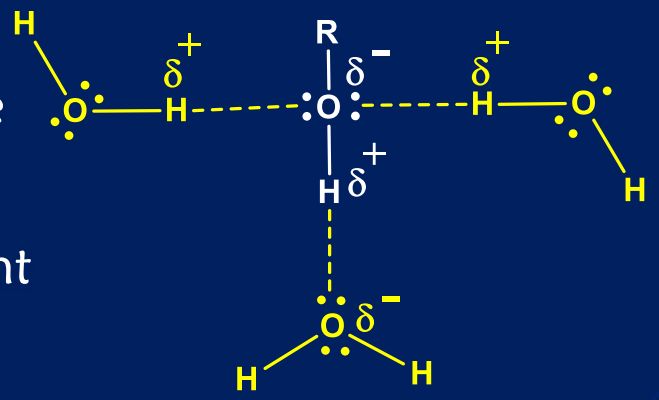
Physical properties

- Lower members are liquids at room temperature (methanol, ethanol etc…), highly branched and with more than twelve carbon atoms alcohols are solids.
- The boiling points of alcohols are higher than those alkanes, alkenes and alkyl halides of similar molar mass this is due existing of intermolecular hydrogen bonding in alcohols.



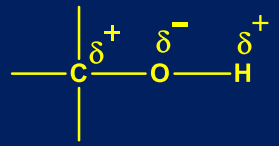


- **Solubility:** lower members of alcohols are dissolve in water this is due to hydrogen bonds are formed between the –OH group of alcohol molecule and the –OH group of water molecule.
- Solubility of alcohols in water decreases with the increasing length of carbon chain. (hydrophobic nature↑)
- In general molecules with more branched will be more soluble and will have lower boiling point than the straight chain isomers.



Chemical properties

- Alcohols contains ionic C-O and O-H bonds hence these are shown three type of reactions.



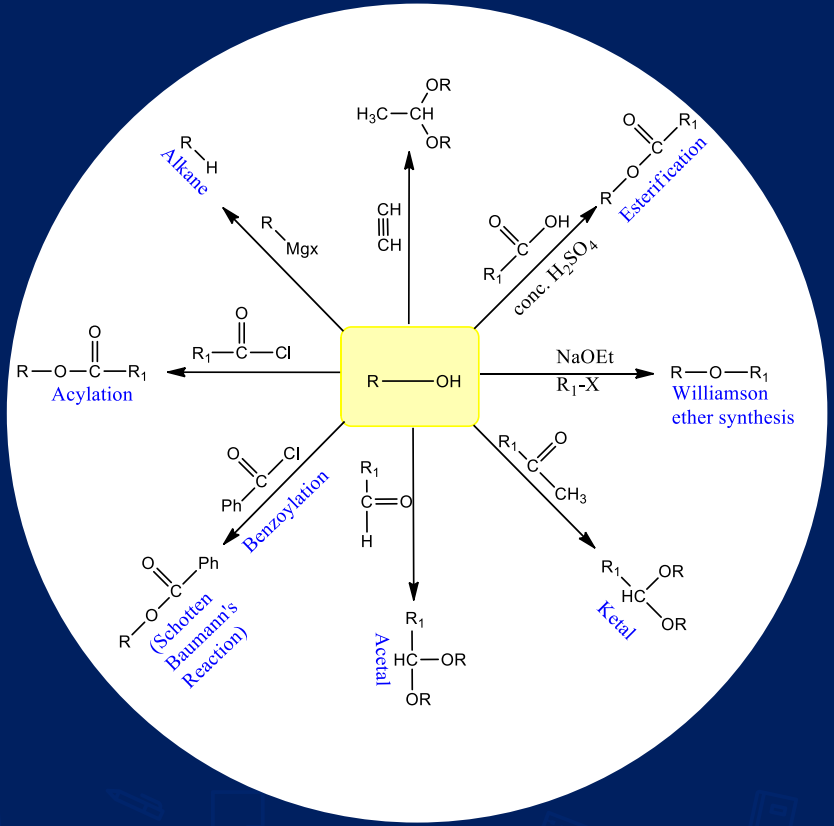
a) Reactions involving cleavage of –O-H

b) Reactions involving cleavage of -C–O

c) Reactions involving complete molecule of alcohol

a) Reactions involving cleavage of –O-H:

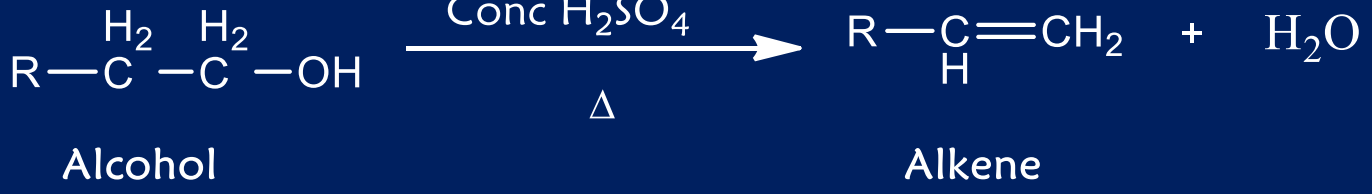
Reactivity order is $CH_3OH > CH_3CH2OH > (CH_3)_2CHOH > (CH_3)_3COH$



b) Reactions involving cleavage of -C–O bond:

Reactivity order: $(CH_3)_3COH > (CH_3)_2CHOH > CH_3CH_2OH > CH_3OH$

- **Dehydration of alcohols:** Heating of alcohols in the presence of an acid catalyst (like Conc. H_2SO_4, H_3PO_4, and P_2O_5 etc.) at 170^0C - 200^0C alkenes are formed.



Mechanism:

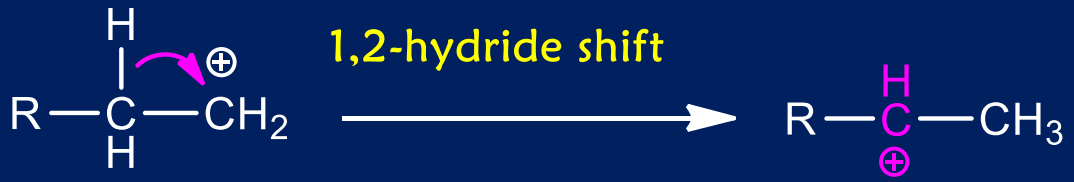
Step-1 Protonation of alcohols

Alkyl Oxonium ion

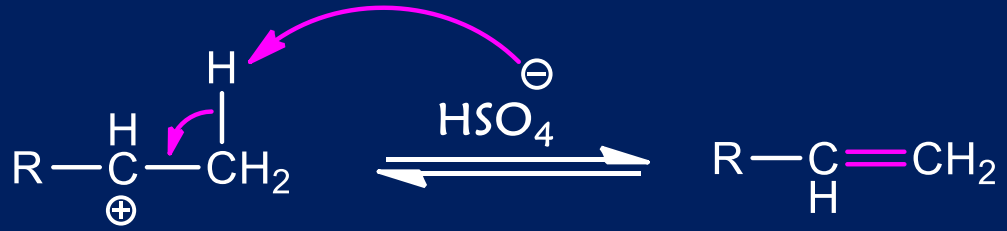
Step-2 formation of carbocation intermediate

Carbocation

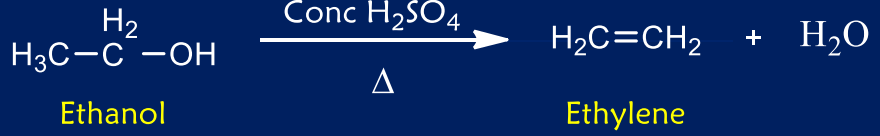
Step-3: 1,2-hydride shift or 1,2-alkyl shift

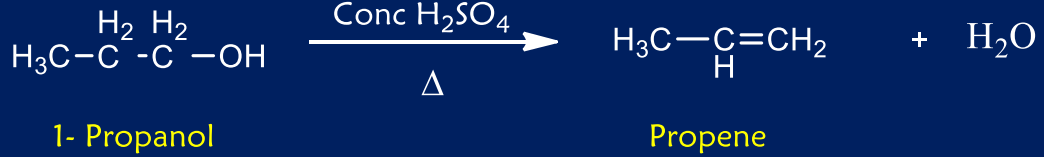


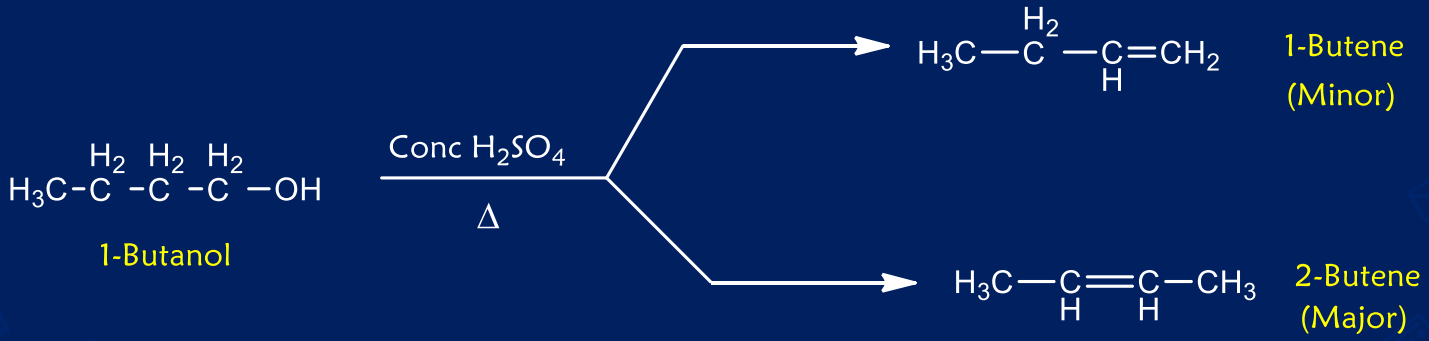
Step-4: Formation of alkene



Ex:

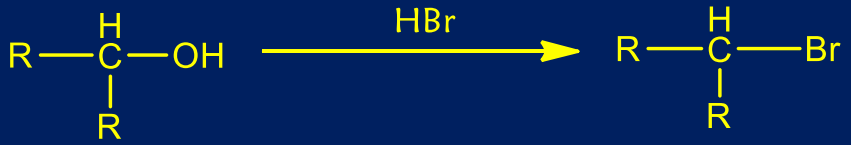

Conc H_2SO_4
Δ
$H_2C=CH_2$ + H_2O
Ethanol
Ethylene


Conc H_2SO_4
Δ
+ H_2O
1- Propanol
Propene


Conc H_2SO_4
Δ
1-Butanol
1-Butene
(Minor)
2-Butene
(Major)

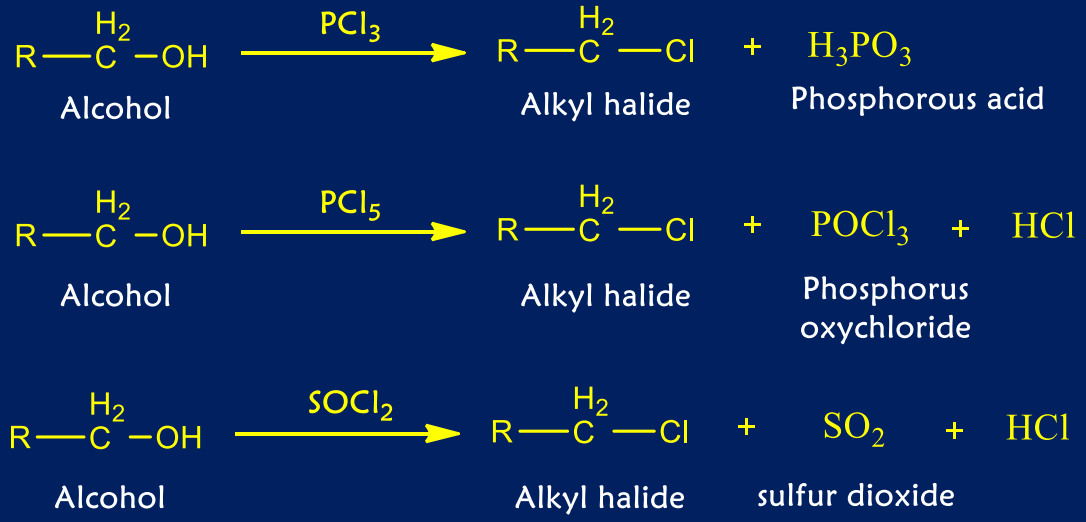
Reaction with halogen acids(HX):

- In this reaction alkyl halides are formed.
- order of reactivity of HX is HI> HBr > HCl > HF.
- Intermediates are carbocations.
- carbocation rearrangements takes place (1,2-hydride shift or 1,2-alkyl shift).



- ## Reaction with Phosphorous and thionyl halides:

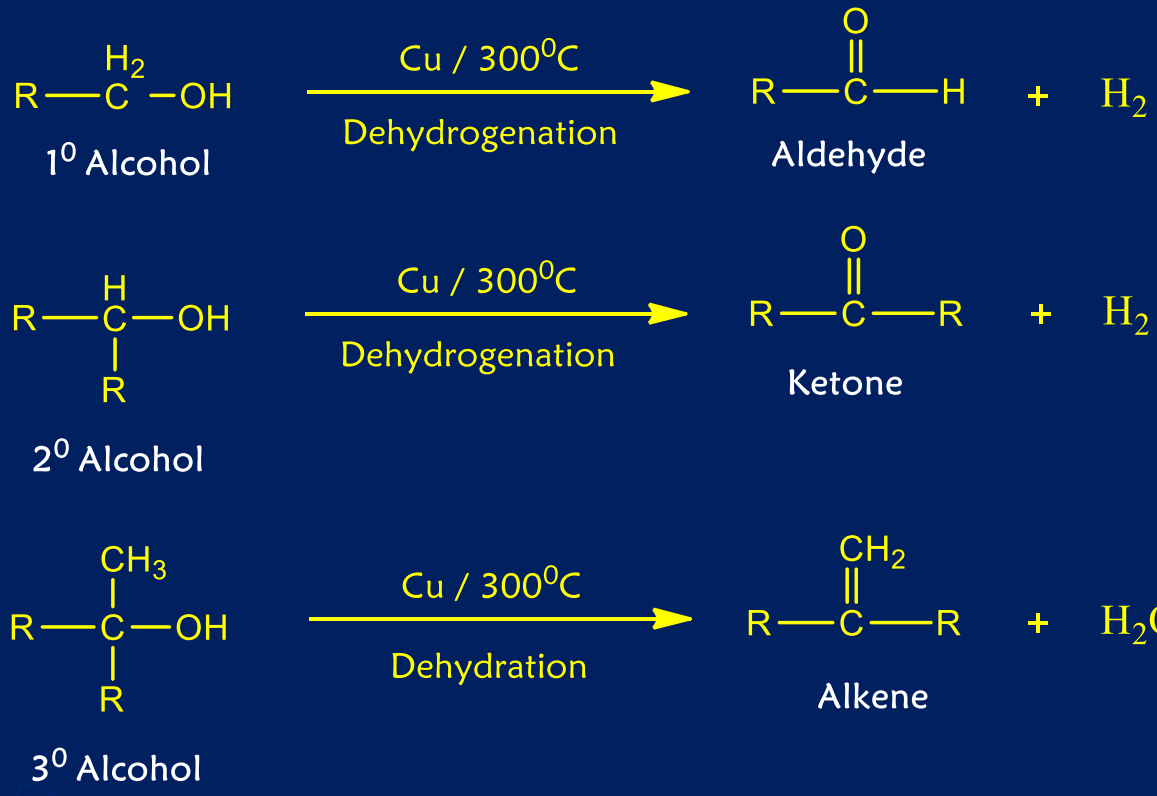
Alcohols react with Phosphorous and thionyl halides to form alkyl halides.



c) Reactions involving complete molecule of alcohol:

- Dehydrogenation: when 1°, 2° and 3° alcohols are passed over hot reduced copper at 300°C, they give different products.

  - This reaction is useful in distinction of 1°, 2° and 3° alcohols.

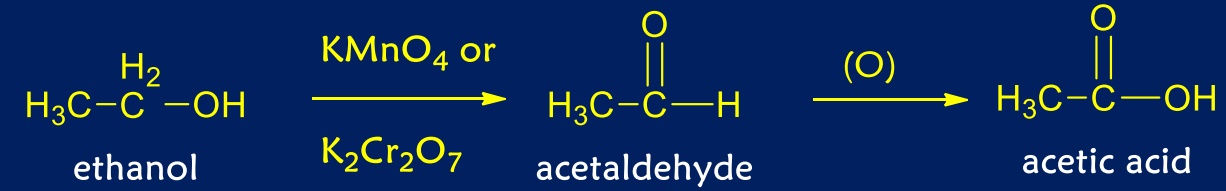

H2
R — C — OH
1⁰ Alcohol
Cu / 300⁰C
Dehydrogenation
O
R — C — H
Aldehyde
+ H2
H
R — C — OH
R
2⁰ Alcohol
Cu / 300⁰C
Dehydrogenation
O
R — C — R
Ketone
+ H2
CH3
R — C — OH
R
3⁰ Alcohol
Cu / 300⁰C
Dehydration
CH2
R — C — R
Alkene
+ H2O

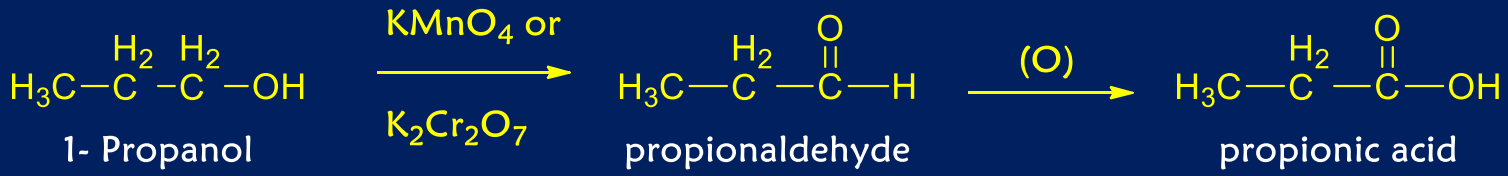
Oxidation of alcohols:

With $KMnO_4$ or $K_2Cr_2O_7$: alcohols are first oxidized to carbonyl compounds (aldehydes, Ketones) and then further oxidized to carboxylic acids

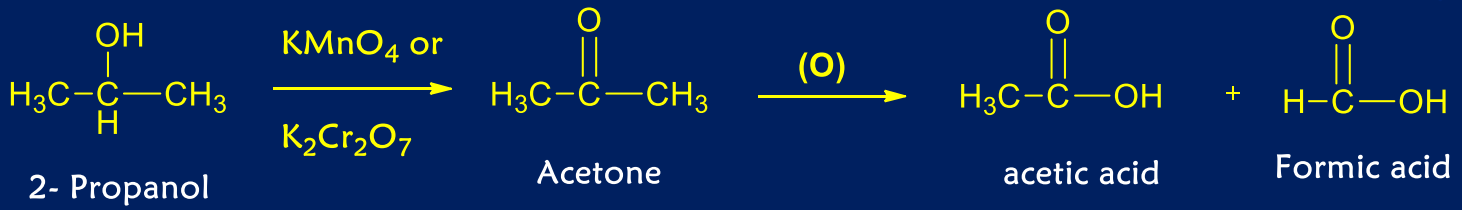
- 1° and 2° alcohols ---------> Carboxylic acids
- 3° alcohols ----------> No reaction
- This reaction is useful in distinction of 1°, 2° and 3° alcohols

Primary alcohol:





secondary alcohol:



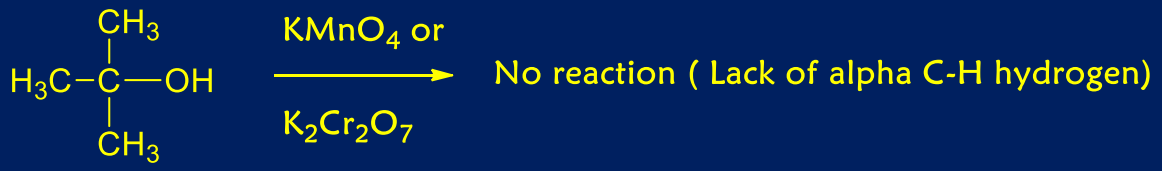
2- Propanol

Acetone

acetic acid

Formic acid

Tertiary alcohol:



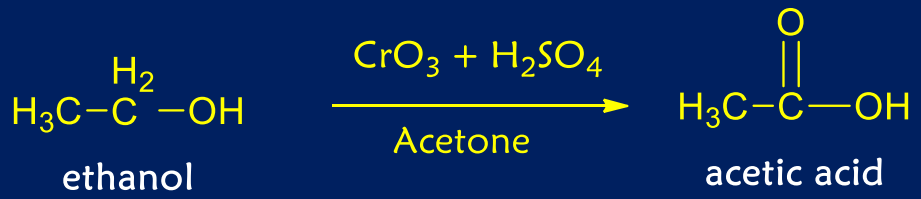
No reaction (Lack of alpha C-H hydrogen)

tertiary Butanol

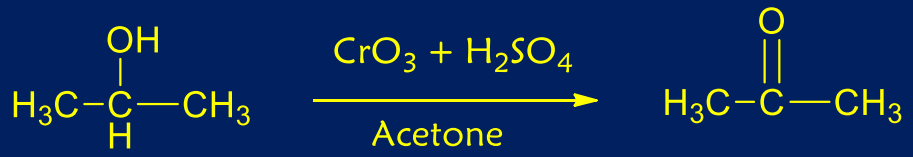
Oxidation with Jones reagent ($CrO3 + H_2SO_4 = H_2CrO_4$):

- Jones reagent is used for the oxidation of primary and secondary alcohols to carboxylic acids and ketones, respectively.
- tertiary alcohols do not undergo oxidation due to lack of α C-H hydrogen.

Primary alcohol:



secondary alcohol:



2- Propanol

Acetone

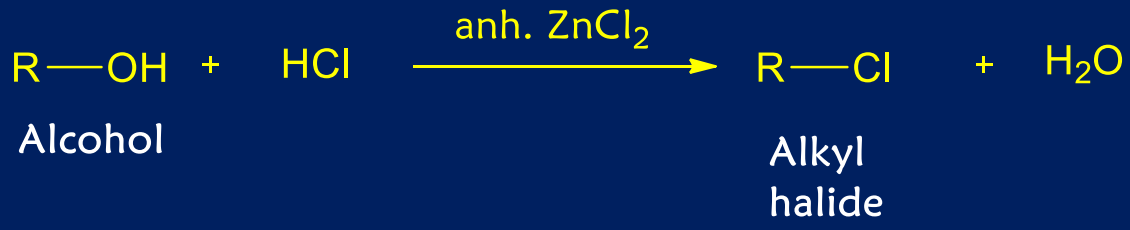
Tertiary alcohol:

tertiary Butanol

No reaction (Lack of alpha C-H hydrogen)

Lucas reagent:

- Lucas reagent is a solution of anhydrous $ZnCl_2$ and conc. HCl.
- This reagent is useful to identification of 1°, 2° and 3° alcohols.
- This reaction is an nucleophilic substitution reaction (SN1) in which a chloride replaces hydroxyl group resulting products are alkyl halides. Generally alkyl halides are insoluble in water it causes the solution become turbid



Primary alcohol

Primary alcohols react very slowly with Lucas reagent so turbidity is not produced instantaneously it takes some hours of time.

Secondary alcohol

Secondary alcohols give turbidity after 5 to 6 min of time with Lucas reagent

Tertiary alcohol

Tertiary alcohols give turbidity instantaneously with Lucas reagent

Thank you