UNIT 10

ALCOHOLS

NEB Syllabus:

- *Introduction, classification, nomenclature and isomerism*
- *Distinction of primary, secondary and tertiary alcohol by Victor Meyer's Method*
- *Preparation of monohydric alcohols from (i) Haloalkanes (ii) primary amines (iii) Esters (iv) Grignard's reagents using aldehydes and ketones*
- *Industrial preparation of ethanol from (i) Oxo-process (ii) Hydroboration-Oxidation process (iii) Fermentation of sugar*
- *Absolute alcohol, Rectified spirit, Power alcohol, Denatured alcohol (Methylated spirit) and alcoholic beverage.*
- *Physical properties of monohydric alcohols*
- *Chemical properties of monohydric alcohols*
  - *Reaction with HX, PX3, PCl5 and SOCl2*
  - *Action with reactive metals like Na, K and Li*
  - *Esterification process*
  - *Dehydration of alcohols*
  - *Oxidation of primary, secondary and tertiary alcohol with oxidizing agents.*
  - *Reduction of alcohols (Catalytic dehydrogenation)*
  - *Laboratory test of ethanol*

Introduction

Hydroxy derivatives of aliphatic hydrocarbons are called aliphatic alcohols.
Aliphatic alcohols are represented by R – OH.
Examples:

CH3 – CH2 – OH CH3 – CH – OH CH3
Ethanol | |
CH3 CH3 - C – OH
Propan-2-ol |
CH3
2-methylpropan-2-ol

Classification of Alcohols:

On the basis of number of hydroxy (–OH) group present in alcohol, they are classified into following types;

1. Monohydric (Monohydroxy) alcohols:

Alcohols containing only one – OH group per molecule.

Monohydric alcohols are further classified into primary, secondary and tertiary alcohols according to the type of carbon in which the – OH group is attached.

a) Primary (1o) alcohols:

Alcohols in which the – OH group is attached to a primary carbon atom.

CH3 – CH2 – OH CH3 - CH – CH2 – OH
Ethanol |
CH3
2-methylpropan-1-ol

b) Secondary (2o) alcohols:
Alcohols in which the – OH group is attached to a secondary carbon atom.

CH3 – CH – OH CH3 – CH2 – CH – CH3
| |
CH3 OH
Propan-2-ol Butan-2-ol

c) Tertiary (3o) alcohols:
Alcohols in which the – OH group is attached to a tertiary carbon atom.
CH3 CH3
| |
CH3 – C – OH CH3 – CH2 – C – OH
| |
CH3 CH3
2-methylpropan-2-ol 2-methylbutan-2-ol

2. Dihydric (Dihydroxy) alcohols:
Alcohols containing two – OH group per molecule.

CH2 – OH
|
CH2 – OH
Ethane-1,2-diol
(Ethylene glycol)

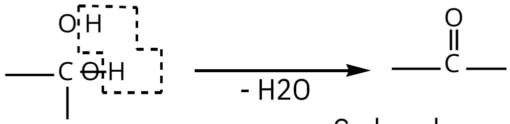
3. Trihydric (Trihydroxy) alcohols:
Alcohols containing three – OH group per molecule.

CH2 – OH
|
CH – OH
|
CH2 – OH
Propane-1,2,3-triol
(Glycerol)

4. Polyhydric (Polyhydroxy) alcohols:
Alcohols containing more than three – OH group per molecule.

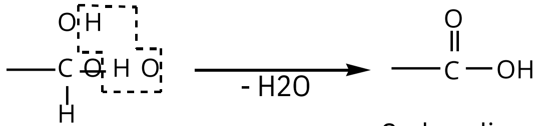
CH2 – OH
|
CH – OH
|
CH – OH
|
CH2 – OH
Butane-1,2,3,4-tetraol

NOTE: It may be noted that more than one – OH group cannot be present on the same carbon atom. In such case, compound will be highly unstable and will easily loses water molecule.
If two – OH groups are present on the same carbon atom, the molecule loses water molecule and converted into carbonyl compound (aldehyde or ketone)



Unstable Carbonyl compound

If three – OH groups are present on the same carbon atom, the molecule loses water molecule and converted into carboxylic acid.



Unstable Carboxylic acid

Nomenclature:

IUPAC Name: Alk + an + ol

Common Name: Alk + yl + alcohol

S.N.	Formula	IUPAC Name	Common Name
1.	CH3 – OH	Methanol	Methyl alcohol
2.	CH3 – CH2 – OH	Ethanol	Ethyl alcohol
3.	CH3 – CH2 – CH2 – OH	Propanol	n-propyl alcohol
4.	CH3 – CH – OH | CH3	Propan -2-ol	iso-propyl alcohol
5.	CH3 – CH2 – CH2 – CH2 – OH	Butanol	n-butyl alcohol
6.	CH3 – CH – CH2 – OH | CH3	2-methyl propanol	iso-butyl alcohol
7.	CH3 – CH2 – CH – OH | CH3	Butan-2-ol	sec-butyl alcohol
8.	CH3 | CH3 – C – OH | CH3	2-methylpropan-2-ol	tert-butyl alcohol
9.	CH2 – OH | CH2 - OH	Ethane-1,2-diol	Glycol
10.	CH2 – OH | CH – OH | CH2 - OH	Propane-1,2,3-triol	Glycerol

Isomerism in alcohols:

Alcohols exhibit following three types of structural isomerism.

1. Chain isomerism:

Isomers differ in the length of the carbon chain. Alcohols containing four or more carbon atoms exhibit chain isomerism.

Chain isomers of $C_4H_{10}O$ are,

$CH_3 – CH_2 – CH_2 – CH_2 – OH$ $CH_3 – CH – CH_2 – OH$

|

Butan-1-ol CH_3

2-methylpropan-1-ol

2. Position isomerism:

Isomers differ in the position of – OH group in the carbon chain. Alcohols containing three or more carbon atoms exhibit position isomerism.

Position isomers of C_3H_8O are,

$CH_3 – CH_2 – CH_2 – OH$ $CH_3 – CH – OH$

Propan-1-ol |

CH_3

Propan-2-ol

3. Functional isomerism:

   Isomers differ in the functional group. Alcohols containing two or more carbon atoms exhibit functional isomer.
   Functional isomers of C_2H_6O are,

   $CH_3 – CH_2 – OH$ $CH_3 – O – CH_3$

   Ethanol Methoxymethane
   (Ethyl alcohol) (Dimethyl ether)
   (Alcohol) (Ether)

<u>Distinction of Primary, Secondary and Tertiary alcohols by Victor Meyer Method:</u>

Primary, secondary and tertiary alcohols can be distinguished by Victor Meyer's method. This method involves the following steps,

Step 1: The given alcohols are treated with red phosphorous and iodine (Red P4 + I2), which converts alcohols into respective iodoalkanes.

Step 2: The iodoalkanes are treated with silver nitrite (AgNO2), which converts iodoalkanes into respective nitroalkanes.

Step 3: The nitroalkanes are treated with nitrous acid, HNO2 (NaNO2 + dil.HCl) which forms respective compounds.

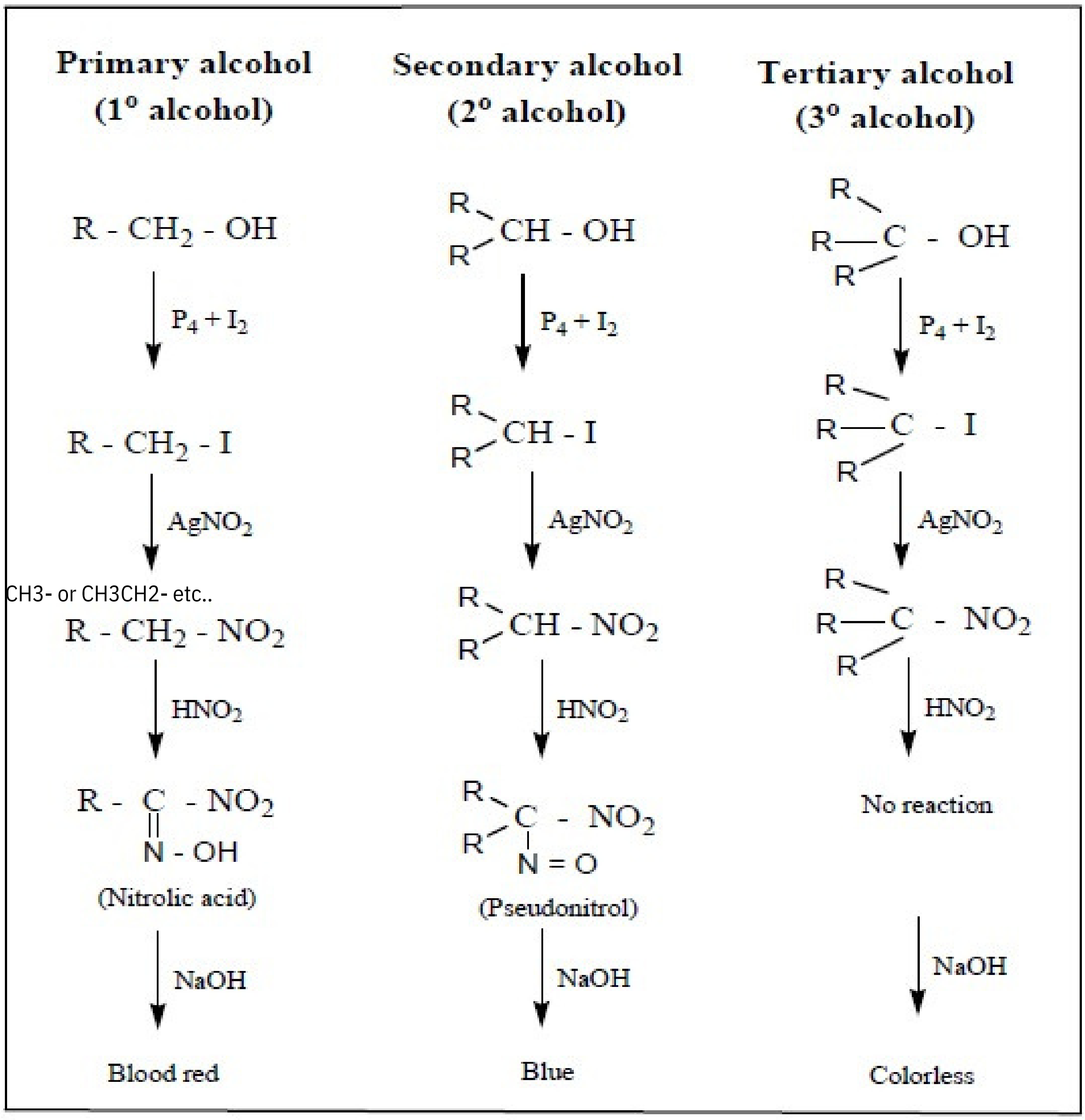
Step 4: Finally, aqueous NaOH or KOH is added to the resulting solution then different color are formed.

If the color is blood red, the given alcohol is primary alcohol.

If the color is blue, the given alcohol is secondary alcohol.

If it is colorless, the given alcohol is tertiary alcohol.

Reactions involved in Victor Meyer's method.



Where R = CH3- or CH3CH2- etc..

General Methods of Preparation of Monohydric Alcohols:

1. From Primary amines:

$$\underset{1^\circ\ \text{amine}}{R-NH_2} + \underset{\text{Nitrous acid}}{HNO_2} \xrightarrow[(0^\circ C - 5^\circ C)]{NaNO_2 + HCl} \underset{\text{Alcohol}}{R-OH} + H_2O + N_2$$

$$\underset{\text{Ethanamine}}{CH_3-CH_2-NH_2} + \underset{\text{Nitrous acid}}{HNO_2} \xrightarrow[(0^\circ C - 5^\circ C)]{NaNO_2 + HCl} \underset{\text{Ethanol}}{CH_3-CH_2-OH} + H_2O + N_2$$

2. From haloalkanes:

$$\underset{\text{Haloalkane}}{R-X} \xrightarrow{\text{aq. NaOH or aq. KOH or moist Ag2O}} \underset{\text{Alcohol}}{R-OH}$$

$$\underset{\text{Chloroethane}}{CH3 - CH2 - Cl + aq. NaOH} \longrightarrow \underset{\text{Ethanol}}{CH3 - CH2 - OH + NaCl}$$

AgO H 2+2O

$$\underset{\text{1-bromopropane}}{CH3 - CH2 - CH2 - Br + AgOH} \longrightarrow \underset{\text{Propan-1-ol}}{CH3 - CH2 - CH2 - OH + AgBr}$$

CH3 - CH - CH3 + aq. KOH ⟶ CH3 - CH - CH3 + KCl

Cl | | OH

2-chloropropane   Propan-2-ol

3. By hydrolysis of esters:

a) Hydrolysis in acidic medium:

$$\underset{\text{Ester}}{R-\overset{O}{\overset{\|}{C}}-\boxed{O-R' + H}} \underset{\text{Water}}{-OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Carboxylic acid}}{R-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{Alcohol}}{R'-OH}$$

O
HO " "

CH3 - C - O - CH2 - CH3 + H - OH CH3 - C - OH + CH3 - CH2 - OH

Ethylethanoate Water Ethanoic acid Ethanol

b) Hydrolysis in alkaline medium:

O O

NaOH " "

CH3 - C - O - CH2 - CH3 + H2O CH3 - C - ONa + CH3 - CH2 - OH

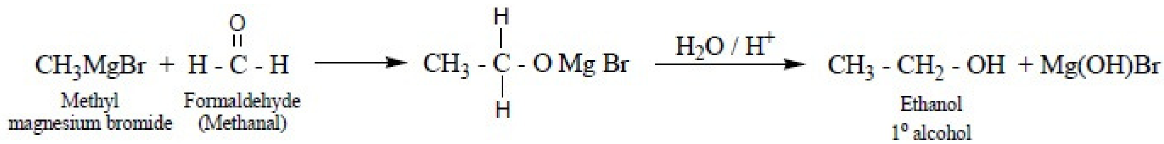
Ethylethanoate Sodiumethanoate Ethanol

4. From Grignard reagents:

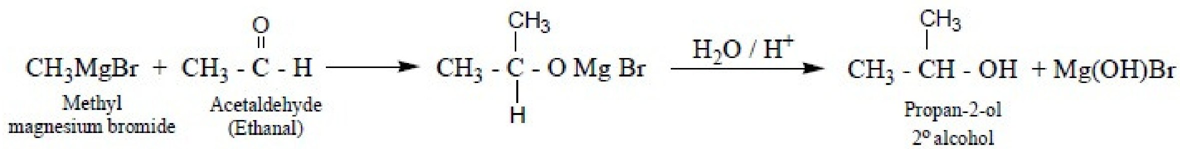
Grignard reagent (RMgX) forms addition product with aldehyde or ketone. The addition compound on acidic hydrolysis gives corresponding alcohol.

➢

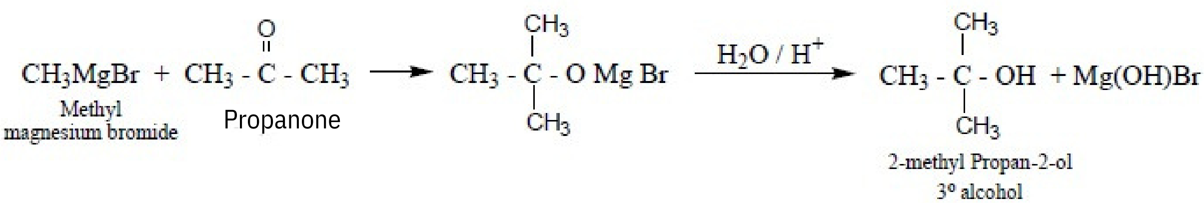
Formaldehyde (Methanal) gives primary alcohol.



➢ All aldehydes other than formaldehyde give secondary alcohol.



➢ Ketones give tertiary alcohol.

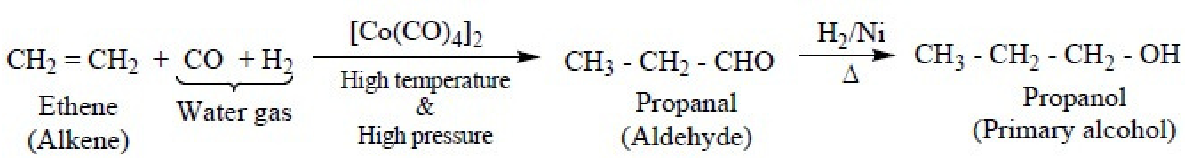


Industrial Method of Preparation of Alcohol:

1. By Oxo process:

   Alkene reacts with water gas (CO + H2) in presence of dicobalt octacarbonyl, [Co(CO)4]2 as a catalyst under high temperature and pressure to give aldehyde (having one carbon atom greater than alkene), which on catalytic hydrogenation gives primary alcohol.

   i.e.



2. By Hydroboration-Oxidation of alkenes:

   Alkene reacts with diborane to give trialkyl boron, which on oxidation with alkaline hydrogen peroxide gives alcohol.

$$3CH_2 = CH_2 + 1/2\ (BH_3)_2 \longrightarrow (CH_3 - CH_2)_3B$$

Ethene Diborane — Triethylboron

$$(CH_3 - CH_2)_3B + 3H_2O_2 \xrightarrow{OH^-} 3\ CH_3 - CH_2 - OH + H_3BO_3$$

Triethylboron Hydrogenperoxide — Ethanol — Boric acid

3. <u>By Fermentation:</u>

The process of decomposition of complex organic compounds into simpler molecules in presence of enzyme secreted by microorganism like yeast is called fermentation.

Fermentation process is widely used to manufacture ethyl alcohol from carbohydrates.

Preparation of ethyl alcohol from sugar (Sucrose)

$$\underset{\text{Sucrose or sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose / Fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2$$

Preparation of ethyl alcohol from starch:

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{n(C_{12}H_{22}O_{11})}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2$$

Some Terminology

Absolute alcohol: 100% pure ethyl alcohol

Rectified spirit: 95% ethyl alcohol

Denatured alcohol (Methylated spirit): Ethyl alcohol containing poisonous substance likes methyl alcohol, acetone, pyridine etc. which is unfit for drinking is called denatured alcohol.

Wood spirit: Methyl alcohol is called wood spirit. It is poisonous and colorless.

Power alcohol: Mixture of 80% petrol & 20% absolute alcohol is called power alcohol. It is used as fuel.

Alcoholic Beverage: Liquors use for drinking purposes and contain ethyl alcohol as a principal intoxicating agent are called alcoholic beverages. These are two types; Undistilled and distilled.

Physical Properties of Monohydric alcohols

a) Physical Character

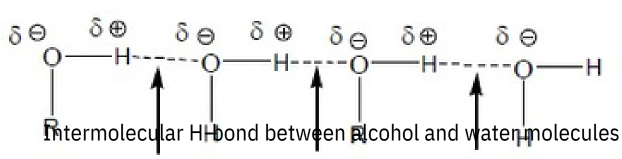
State: Lower members up to C11 are liquid and higher member above C11 are solid

Color: Colorless

Odor: Lower members up to C11 have characteristic alcoholic smell and higher member above C11 are odorless.

1. Solubility:

Lower members of alcohols are soluble in water due to the formation of intermolecular H-bond with water molecule.

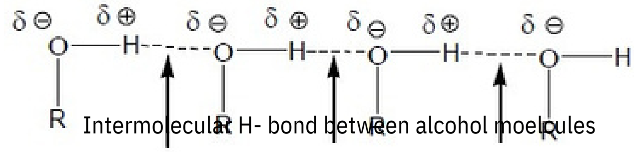


Intermolecular H-bond between alcohol and water molecules

Higher alcohols i.e. alcohols with larger alkyl groups are less or insoluble due to increase non-polar water repelling nature of alkyl groups.

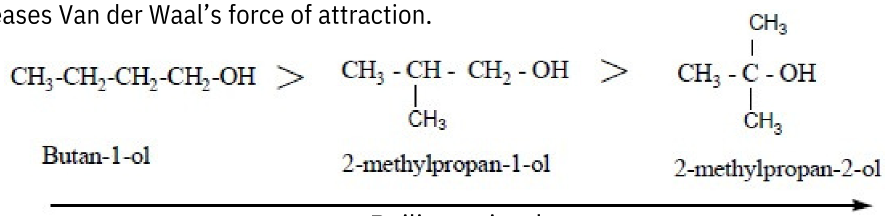
2. Boiling point:

Alcohols have higher boiling point than alkane, haloalkane & isomeric ether because alcohol can form intermolecular H-bonds with each other whereas alkane, haloalkane and ether cannot.



Intermolecular H- bond between alcohol moelcules

In isomeric alcohol, boiling point decreases with increasing branching. Branching decreases the surface area, which decreases Van der Waal's force of attraction.



Boiling point decrease

Within homologous series, boiling point increases with increase in molecular mass.

$$CH_3\text{-}OH < CH_3\text{-}CH_2OH < CH_3\text{-}CH_2\text{-}CH_2\text{-}OH\ldots\ldots$$

$$\xrightarrow[\text{Boiling point increase}]{}$$

Chemical properties of Monohydric alcohols:

Alcohols are quite reactive than haloalkane because the alcohols has two reactive (polar) covalent bonds, the C– O bond and the O–H bond.

The electronegativity of oxygen is substantially greater than that of carbon and hydrogen. Consequently, the covalent bonds of this functional group are polarized so that oxygen is electron rich (nucleophilic) and both carbon and hydrogen are electron deficient (electrophilic).

The most reactive site in an alcohol molecule is the hydroxyl group, despite the fact that the O–H bond strength is significantly greater than that of the C–C, C–H and C–O bonds.

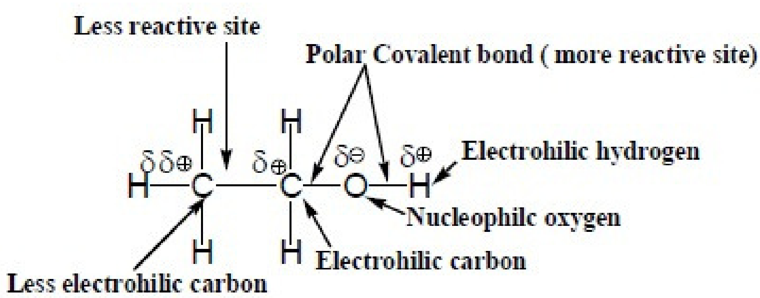


Fig. Polarity in alcohol (Reaction sites in alcohol)

1)Reaction with halogen acids (HX) (Basic nature of alcohol)

$$R\ OH + H\ X \longrightarrow R{-}X + H_2O$$

Alcohol Hydrogen halide Haloalkane

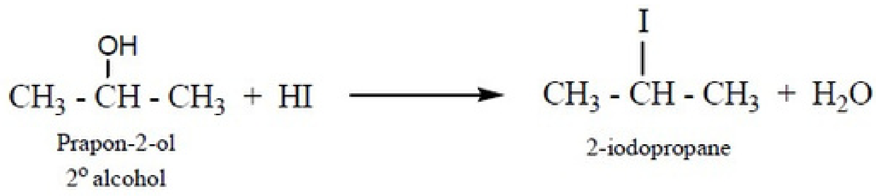
HX= HCl, HBr or HI

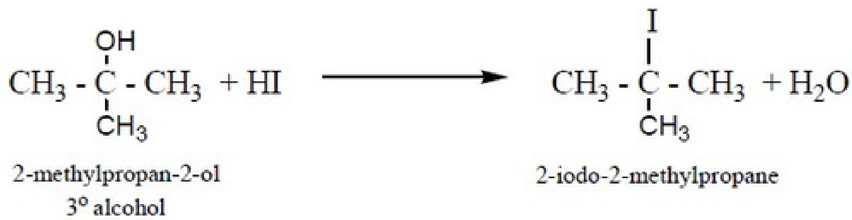
> ***The reactivity of HX*** = HI > HBr> HCl
> ***Reactivity of alcohol towards HX:*** $3^o > 2^o > 1^o$

i) Reaction with HI:

HI reacts with 1^o, 2^o and 3o alcohols without any catalyst.

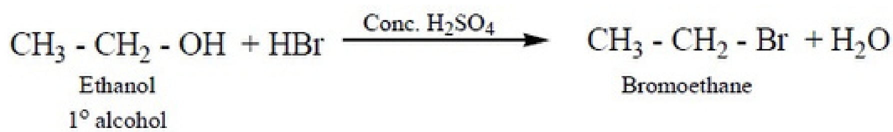
$$\underset{\substack{\text{Ethanol}\\ 1^\circ\ \text{alcohol}}}{CH_3\text{-}CH_2\text{-}OH} + HI \longrightarrow \underset{\text{Iodoethane}}{CH_3\text{-}CH_2\text{-}I} + H_2O$$

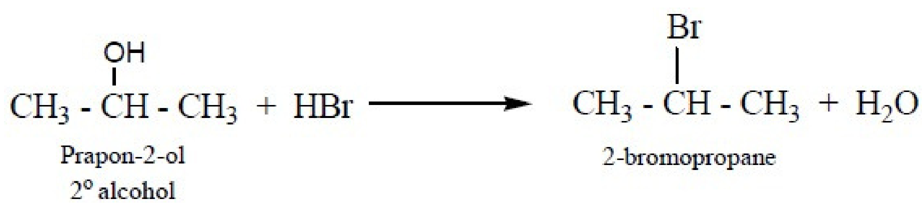


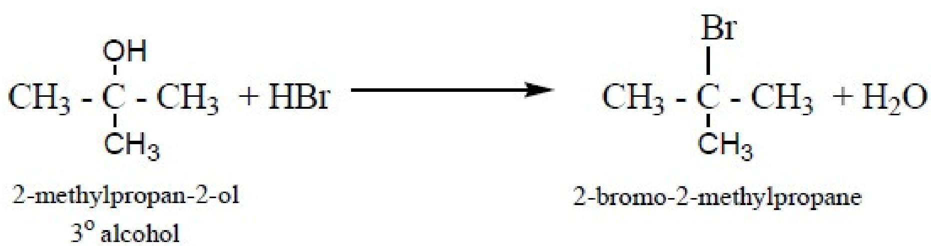


ii) Reaction with HBr:

HBr reacts with 1° alcohols in presence of Conc.H2SO4 as catalyst but it reacts with 2° and 3° alcohols without any catalyst.

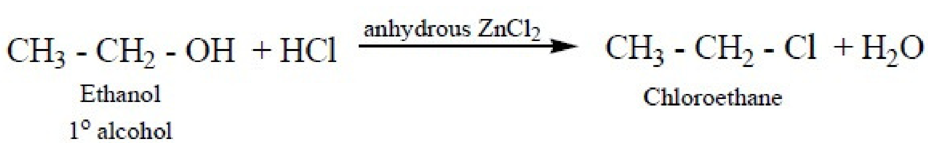


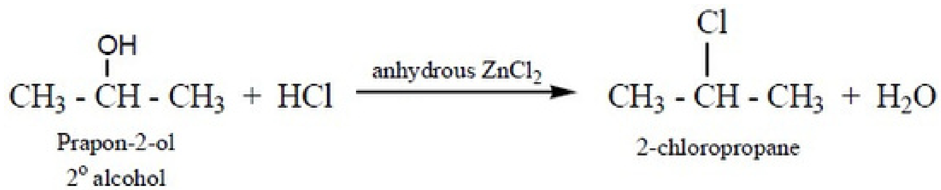


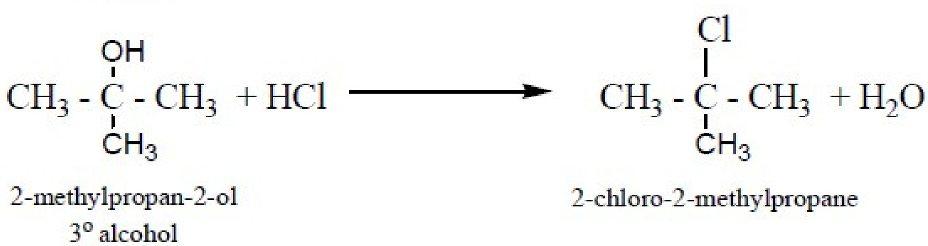


iii) Reaction with HCl:

HCl reacts with 1°and 2° alcohols in presence of Conc.H2SO4 or anhydrous ZnCl2 as catalyst but it reacts with 3° alcohols without any catalyst.







2) Reaction with Phosphorous halides:

$$R-OH + PCl_5 \xrightarrow[\Delta]{} R-Cl + POCl_3 + HCl$$

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} + PCl_5 \xrightarrow[\Delta]{} \underset{\text{Chloroethane}}{CH_3-CH_2-Cl} + \underset{\text{Phosphoryl chloride}}{POCl_3} + HCl$$

$$3\,R-OH + PCl_3 \xrightarrow[\Delta]{} 3\,R-Cl + H_3PO_3$$

$$3\,\underset{\text{Ethanol}}{CH_3-CH_2-OH} + PCl_3 \xrightarrow[\Delta]{} 3\,\underset{\text{Chloroethane}}{CH_3-CH_2-Cl} + \underset{\text{Phosphorous acid}}{H_3PO_3}$$

Note: PBr3 and PI3 are unstable so they are prepared in situ by the reaction of Br2 or I2 with red phosphorous.

3) Reaction with Thionyl chloride (SOCl2):

$$\underset{\text{Alcohol}}{R-OH} + \underset{\text{Thionyl chloride}}{SOCl_2} \xrightarrow[\Delta]{\text{Pyridine}} \underset{\text{Chloroalkane}}{R-Cl} + SO_2 + HCl$$

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} + SOCl_2 \xrightarrow[\Delta]{\text{Pyridine}} \underset{\text{Chloroethane}}{CH_3-CH_2-Cl} + SO_2 + HCl$$

4) Oxidation of alcohol:

Alcohols are oxidized by acidified K2Cr2O7 or Na2Cr2O7 or acidified / alkaline KMnO4 solution i.e. (K2Cr2O7 / H+, Na++−2Cr2O7 / H or KMnO4 / H, KMnO4 / OH).

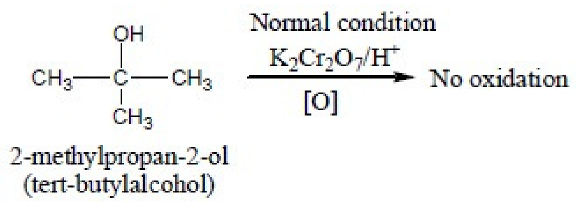
i) Primary alcohols are easily oxidized first into aldehyde & finally into carboxylic acid.

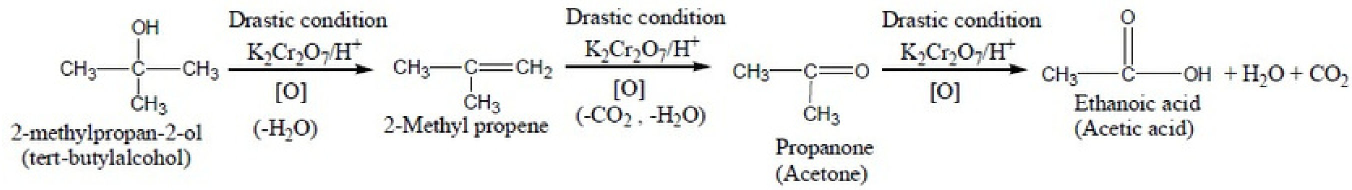
$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[\text{[O]}]{K_2Cr_2O_7/H^+} \underset{\substack{\text{Ethanal}\\\text{(Acetaldehyde)}}}{CH_3-CHO} \xrightarrow[\text{[O]}]{K_2Cr_2O_7/H^+} \underset{\substack{\text{Ethanoic acid}\\\text{(Acetic acid)}}}{CH_3-COOH}$$

ii) Secondary alcohol is easily oxidized into ketones. But, ketone does not oxidized under normal condition. However, under drastic condition (i.e. high temperature and high pressure) ketones are oxidized into carboxylic acid (having one carbon less than ketone).

$$\underset{\substack{\text{Propan-2-ol}\\\text{(Iso- propylalcohol)}}}{CH_3-\overset{\overset{\large OH}{|}}{CH}-CH_3} \xrightarrow[\text{[O]}]{\substack{\text{Normal condtion}\\K_2Cr_2O_7/H^+}} \underset{\substack{\text{Propanone}\\\text{(Acetone)}}}{CH_3-\overset{\overset{\large O}{\|}}{C}-CH_3} \xrightarrow[\text{[O]}]{\substack{\text{Drastic condtion}\\K_2Cr_2O_7/H^+}} \underset{\substack{\text{Ethanoic acid}\\\text{(Acetic acid)}}}{CH_3-\overset{\overset{\large O}{\|}}{C}-OH} + H_2O + CO_2$$

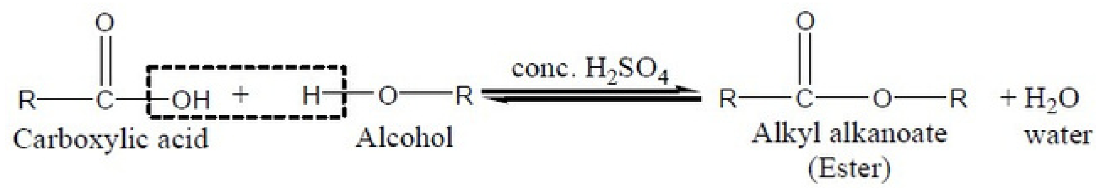
iii) Tertiary alcohol doesnot undergo oxidation under normal condition. However, under drastic condition tertiary alcohol first dehydrate into alkene which further oxidized into ketone and finally into carboxylic acid.



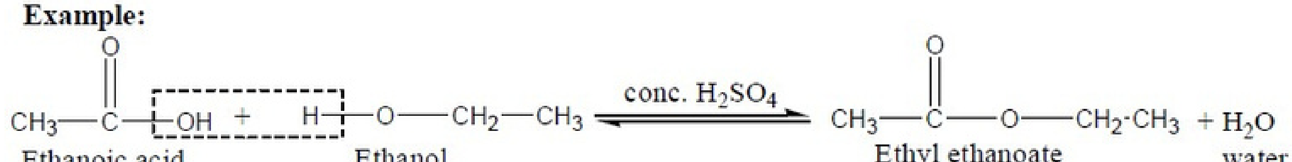


5)Esterification reaction:

When alcohol is heated with carboxylic acid in presence of little Conc. H2SO4 as a catalyst, gives ester. This reaction is called Esterification reaction.



Example:

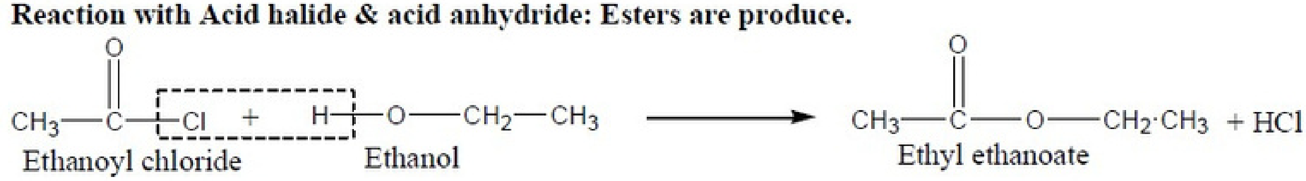


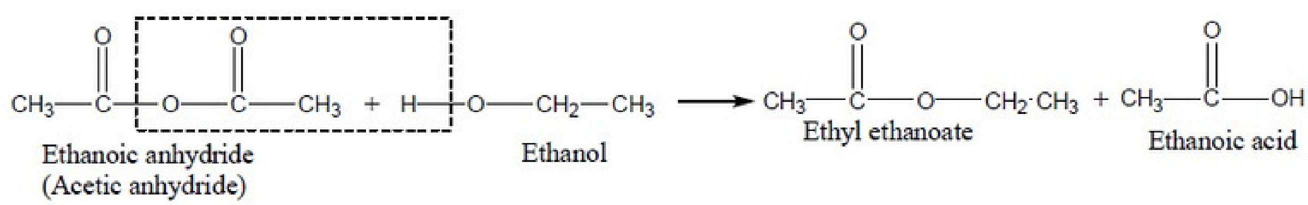
Esters have fruity smell, easily detectable so this reaction can be used to test the presence of alcohol and

➢carboxylic acid. (Esterification test)

Similarly,

Reaction with Acid halide & acid anhydride: Esters are produce.





6)Reaction with active metals (Acidic Nature of alcohol)

Active metals: Alkali metals (more electropositive metals) Li, Na, K

Reactivity of active metals Li < Na < K

CH3—CH2—OH + Na ⟶ CH3— ~~CH2~~ ONa + 1/2 H2
Ethanol Sodium ethoxide
CH3—CH2—OH + K + ⟶ CH3 ~~CH2~~ OK ~~+~~ 1/2 H2
Ethanol Potassium ethoxide
CH3—CH2—OH Li ⟶ CH3— ~~CH2~~ OLi + 1/2 H2
Ethanol Lithium ethoxide

Alcohols are weaker acid because of the presence of polar O—H bond. This polarity in O—H bond arises due to electronegativity difference between the oxygen and hydrogen which allows the separation of H as H+ ion. Since, H+ ion is the measure of acidity of compound as PH = -log [H+].

Comparison of acidic strength of alcohol and water:

Both alcohol and water contain polar O – H group and ionizes in aqueous solution to give H+ ion.

H – O – H ⇔ HO - + H+

R – O – H ⇔ RO - + H+

Alcohols are weaker acid than water because of the presence of electron releasing alkyl group (R), which shows +I effect that increase the electron density in oxygen atom. As a result polarity of O—H bond decreases. Thus, O – H bond of alcohol becomes stronger & release of H as H+ becomes difficult.

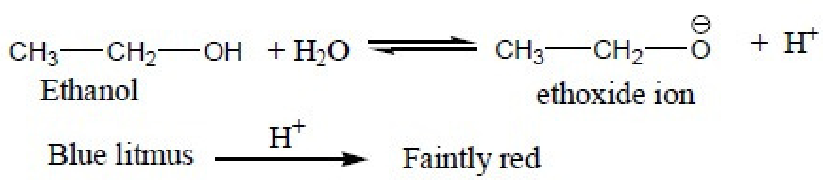
Comparison of acidic strength of primary, secondary and tertiary alcohols:

As the number of electron releasing alkyl groups (+I groups) increases from primary to tertiary, acidity decreases.

For example: 1o alcohol > 2o alcohol > 3o alcohol

Propan-1-ol > Propan-2-ol > 2-methylpropan-2-ol

Litmus test: Alcohol turns blue litmus faintly red.

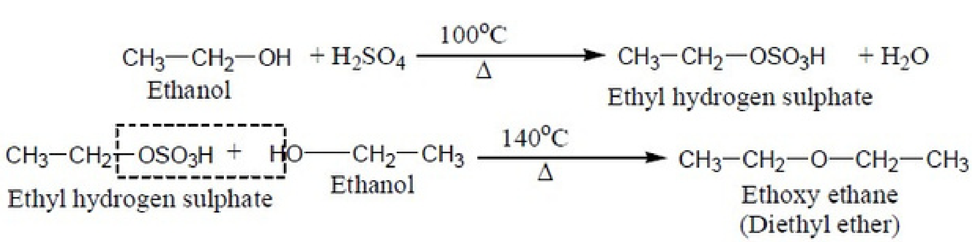


7)Dehydration reaction of alcohols: (Removal of water molecule)

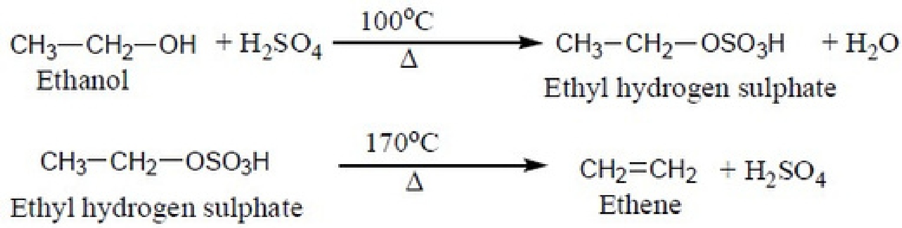
Alcohol can be dehydrated when heated with dehydrating agents like conc. H2SO4.

Product formed (either Alkene or Ether) will depend on the temperature & concentration of alcohol, H2SO4 used in the reaction.

i) When excess alcohol is heated with conc.H2SO4 at 140°C, ether is formed.

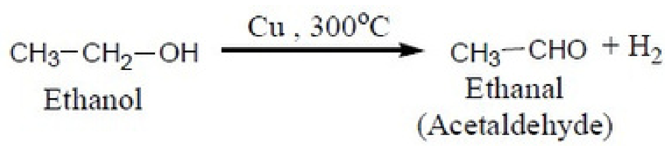


ii) When alcohol is heated with excess conc.H2SO4 at 170°C, alkeneis formed.

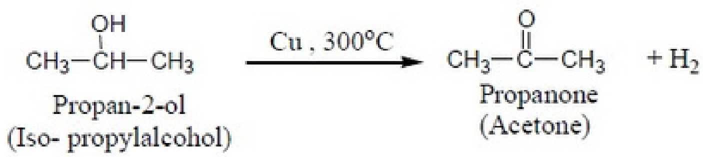


8) Catalytic dehydrogenation: (Removal of hydrogen)

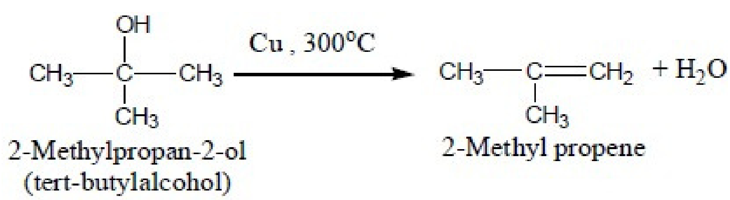
i) Primary alcohols are dehydrogenated into aldehydes



ii) Secondary alcohols are dehydrogenated into ketones

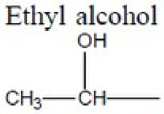


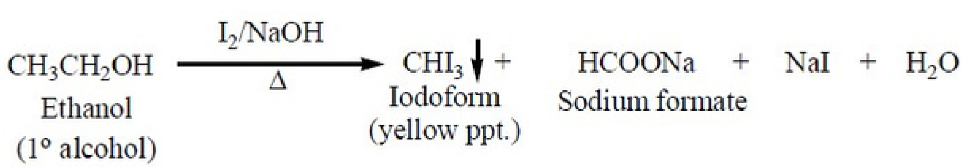
iii) Tertiary alcohols are dehydrated into alkenes.



Lab test of Ethyl alcohol (Ethanol):

1) IODOFORM TEST:

Ethyl alcohol is only the primary alcohol that gives positive iodoform test because ethyl alcohol contains  group. In this test reaction, ethyl alcohol reacts with NaOH and I_2 at around 70°C to produce yellow ppt of iodoform (CHI_3) with characteristics hospital smell.



2) ESTERIFICATION TEST:

Ethyl alcohol reacts with ethanoic acid in presence of Conc. H2SO4 to form ethylethanoate (Ester) which gives fruity smell.