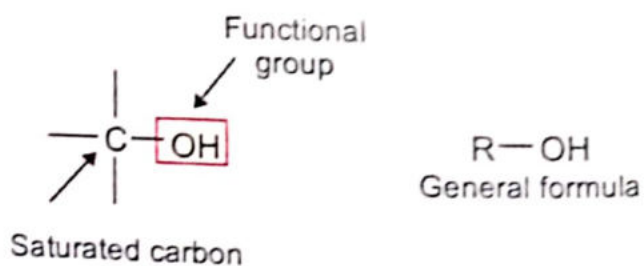


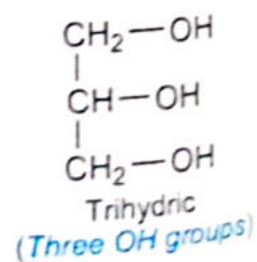
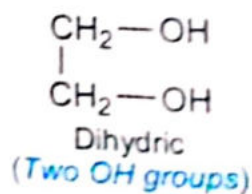
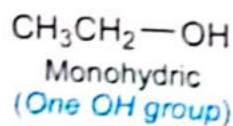


Ethyl alcohol is the *alcohol* of wine, beer and whiskey. Ethyl alcohol may be the first organic chemical routinely manufactured by humans.

**A**lcohols are compounds in which a hydroxyl ( $-OH$ ) group is attached to saturated carbon.



The hydroxyl group is the functional group of alcohols. Alcohols containing one hydroxyl group are called **Monohydric Alcohols**. Alcohols with two, three, or more hydroxyl groups are known as **Dihydric Alcohols**, **Trihydric Alcohols**, and **Polyhydric Alcohols** respectively. For example:

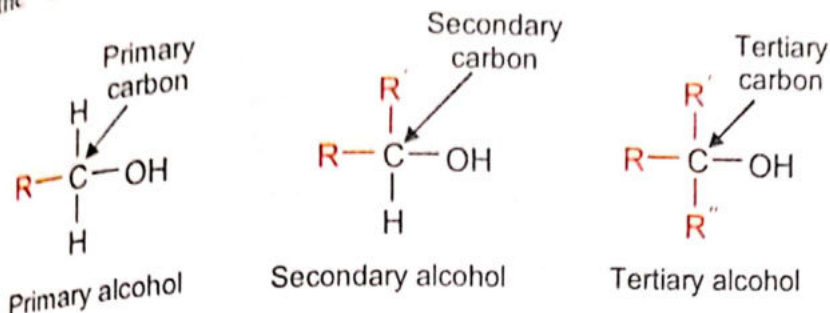


### MONOHYDRIC ALCOHOLS

Monohydric alcohols contain one  $-OH$  group attached to a saturated carbon. They are represented as (R-OH).

## PRIMARY (1°), SECONDARY (2°), AND TERTIARY (3°) ALCOHOLS

Monohydric alcohols are classified as primary (1°), secondary (2°), or tertiary (3°), depending upon whether the -OH group is attached to a primary, a secondary, or a tertiary carbon.



### STRUCTURE

Let us consider methyl alcohol (CH<sub>3</sub>OH) for illustrating the orbital make up of alcohols. In methyl alcohol both oxygen and carbon are  $sp^3$  hybridized. Two of the  $sp^3$  orbitals of oxygen are completely filled and cannot take part in bond formation (Fig. 15.1). The C-O bond in methyl alcohol is formed by overlap of an  $sp^3$  orbital of carbon and an  $sp^3$  orbital of oxygen. The O-H bond is formed by overlap of an  $sp^3$  orbital of oxygen and  $s$  orbital of hydrogen. The C-O-H bond angle is 105°. It is less than the normal tetrahedral angle. This is because the two completely filled  $sp^3$  orbitals of oxygen repel each other. This results in reduction of the bond angle.

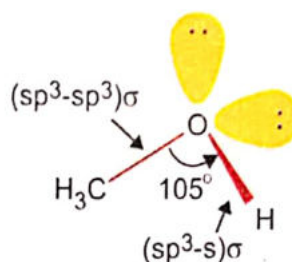
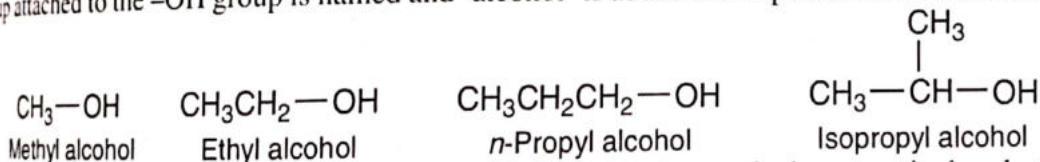


Fig. 15.1 Structure of Methyl alcohol.

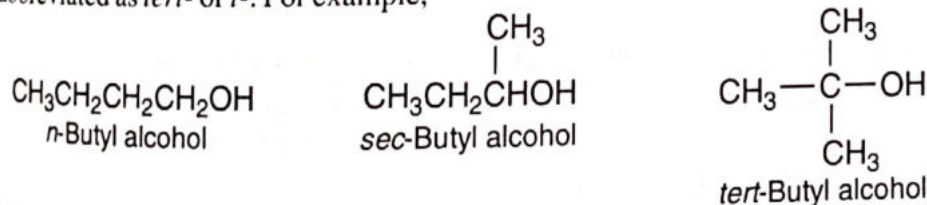
### NOMENCLATURE

Alcohols are named by three systems :

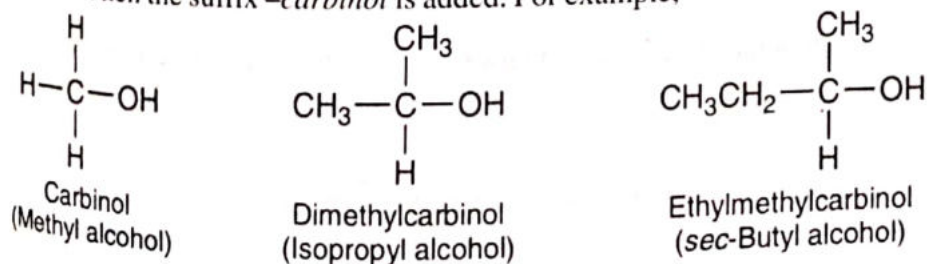
(1) **Common System.** In this system alcohols (R-OH) are named as *Alkyl Alcohols*. The alkyl group attached to the -OH group is named and 'alcohol' is added as a separate word. For example,



As we go higher in the series, it becomes necessary to indicate whether a particular alcohol is primary (1°), secondary (2°), or tertiary (3°). The prefix secondary is abbreviated as *sec-*. The prefix tertiary is abbreviated as *tert-* or *t-*. For example,

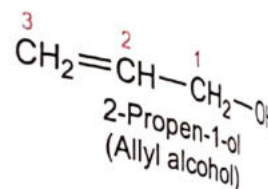
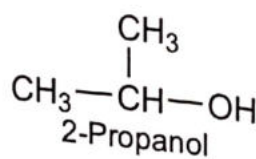
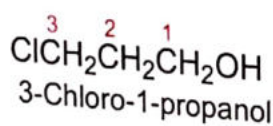
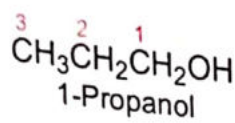
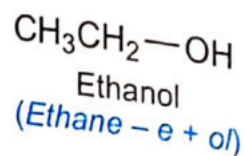
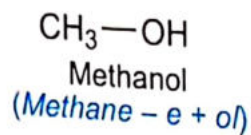


(2) **Carbinol System.** In this system alcohols are considered as derivatives of methyl alcohol which is called *Carbinol*. The alkyl group attached to the carbon carrying the -OH group are named in alphabetic order. Then the suffix *-carbinol* is added. For example,





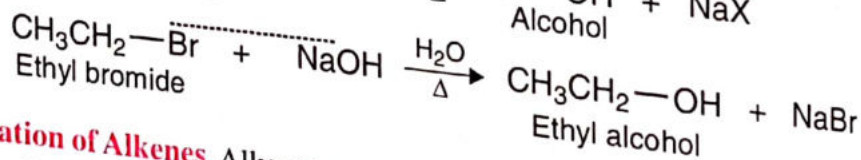
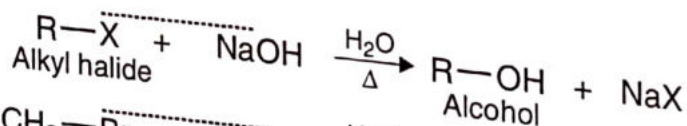
- (3) **IUPAC System.** In this system alcohols are named as *Alkanols*. The IUPAC rules are:
- Select the longest continuous carbon chain containing the  $-OH$  group.
  - Change the name of the alkane corresponding to this chain by dropping the ending  $-ane$  and adding the suffix  $-ol$ .
  - Number the chain so as to give the carbon carrying the  $-OH$  group, the lowest possible number. The position of the  $-OH$  group is indicated by this number.
  - Indicate the positions of other substituents or multiple bonds by numbers.
- The examples given below show how these rules are used :



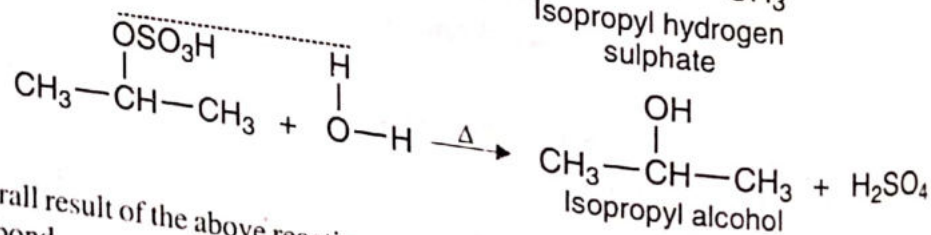
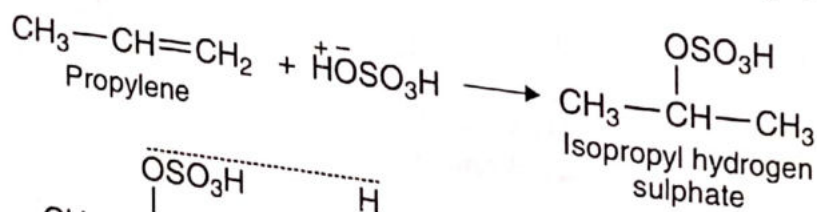
## METHODS OF PREPARATION

Alcohols are prepared by the following methods :

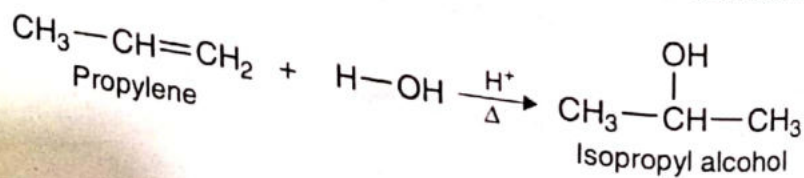
- (1) **Hydrolysis of Alkyl Halides.** Alkyl halides react with aqueous sodium hydroxide to form alcohols.



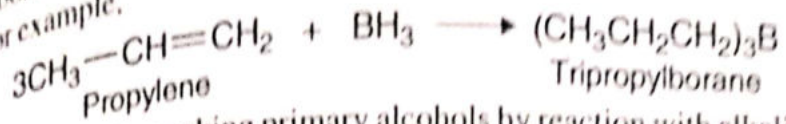
- (2) **Hydration of Alkenes.** Alkenes react with sulfuric acid to produce alkyl hydrogen sulfates (Markovnikov rule is followed). Alkyl hydrogen sulfates on hydrolysis give alcohols. For example:



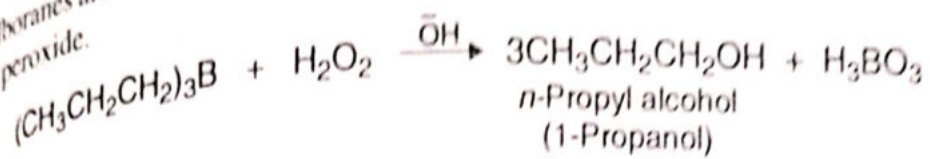
The overall result of the above reactions appears to be Markovnikov addition of  $\text{H}_2\text{O}$  (Hydration) to a double bond.



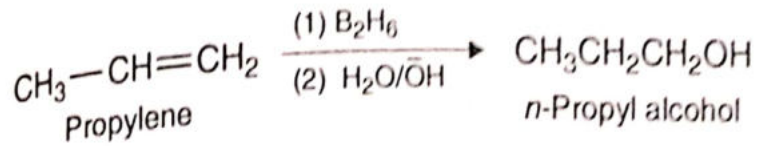
It is not possible to make primary alcohols from alkenes by direct hydration.  
 (7) **Hydroboration-Oxidation of Alkenes.** Alkenes react with diborane,  $B_2H_6$  to form trialkylboranes. Diborane adds as borane,  $BH_3$ . The positive part of  $BH_3$  is the boron, the negative part is hydrogen. For example,



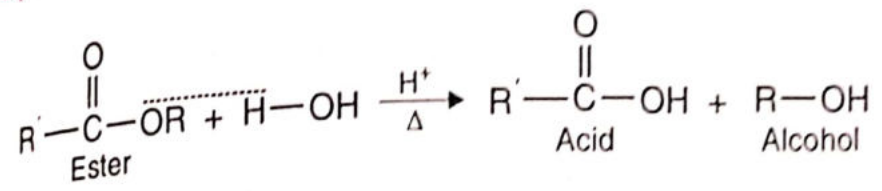
Trialkylboranes are used for making primary alcohols by reaction with alkaline aqueous solution of hydrogen peroxide.



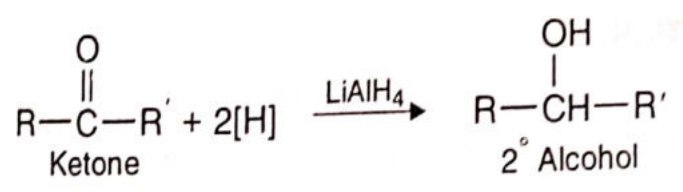
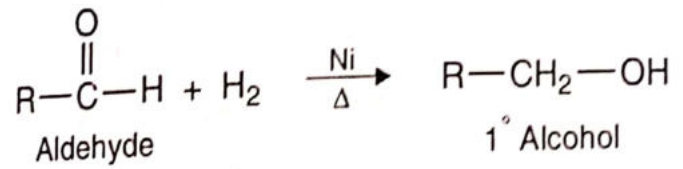
The overall result of the above reactions appears to be *anti*-Markovnikov addition of  $H_2O$  to a double bond.



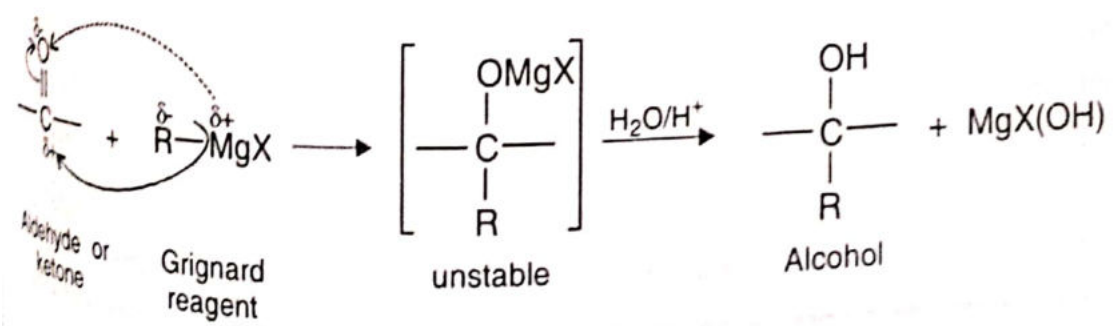
(8) **Hydrolysis of Esters.** Alcohols may be prepared by base or acid-catalyzed hydrolysis of esters.



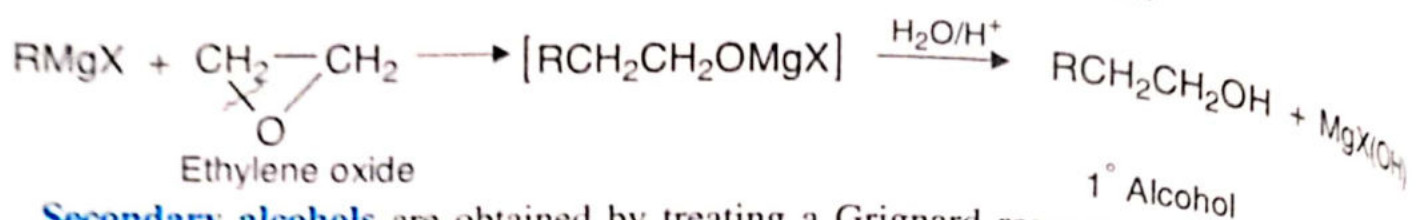
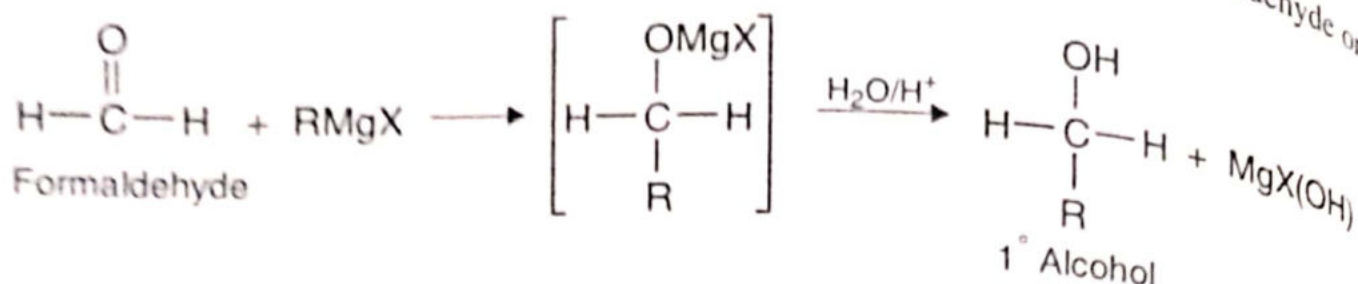
(5) **Reduction of Aldehydes and Ketones.** Aldehydes and ketones can be reduced with  $H_2/Ni$  or from aluminium hydride to form the corresponding alcohols. Aldehydes give primary alcohols. Ketones give secondary alcohols.



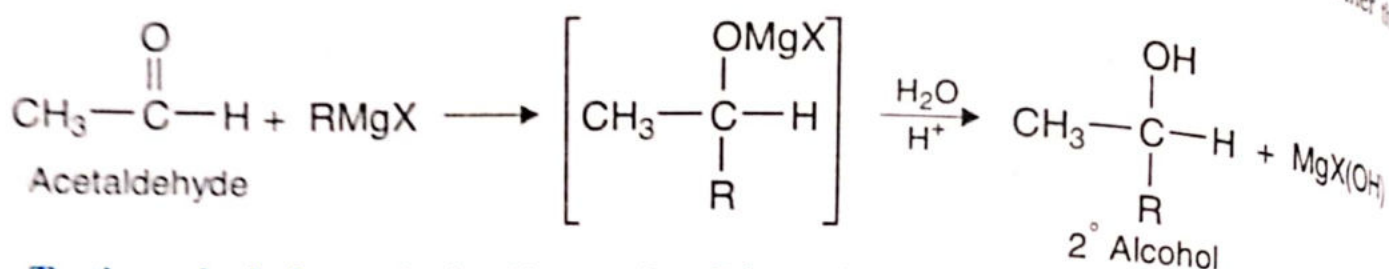
(6) **Addition of Grignard Reagents to Aldehydes and Ketones.** Grignard reagents react with aldehydes or ketones to form an addition compound which on hydrolysis with dilute acid gives the corresponding alcohols.



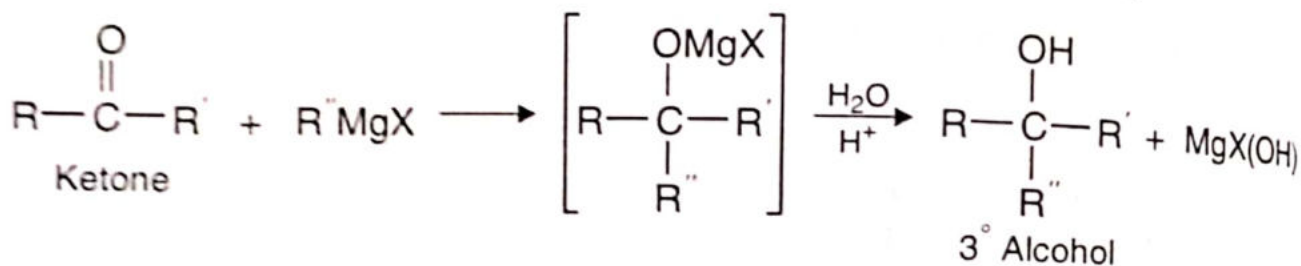
**Primary alcohols** are obtained by treating a Grignard reagent with formaldehyde or ethylene oxide.



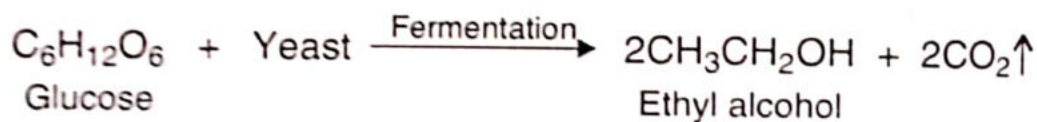
**Secondary alcohols** are obtained by treating a Grignard reagent with aldehydes other than formaldehyde.



**Tertiary alcohols** are obtained by treating Grignard reagents with ketones.



(7) **Fermentation of Carbohydrates.** Some alcohols can be prepared by fermentation of starches and sugars under the influence of suitable microorganisms. For example,



## PHYSICAL PROPERTIES

- (1) Lower alcohols are colorless, toxic liquids. They have a characteristic smell.
- (2) Boiling points of alcohols increase regularly with the increase in the number of carbon atoms (Table 15.1).

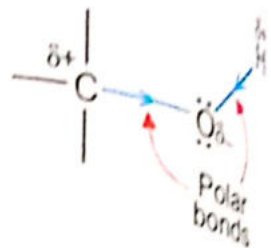


$R = \text{CH}_3$   $\text{CH}_3\text{CH}_2$   $(\text{CH}_2)_3\text{C}$   
 A comparison of boiling points for some alkanes, chloroalkanes, and alcohols.  
 Alcohols generally have the higher boiling points.

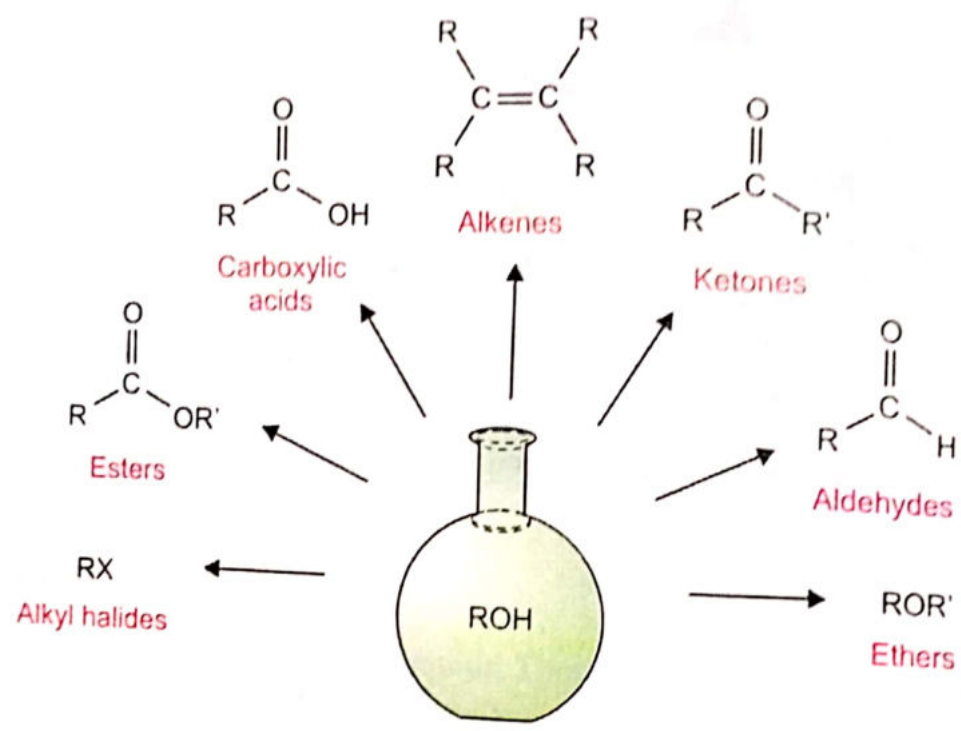
### CHEMICAL PROPERTIES

Alcohols are reactive compounds. They are attacked by polar or ionic reagents. This is because :

- (1) The C-O and O-H bonds of alcohols are polar since oxygen is highly electronegative.
- (2) The oxygen atom of alcohols is an electron-rich centre because it has two unshared pairs of electrons.

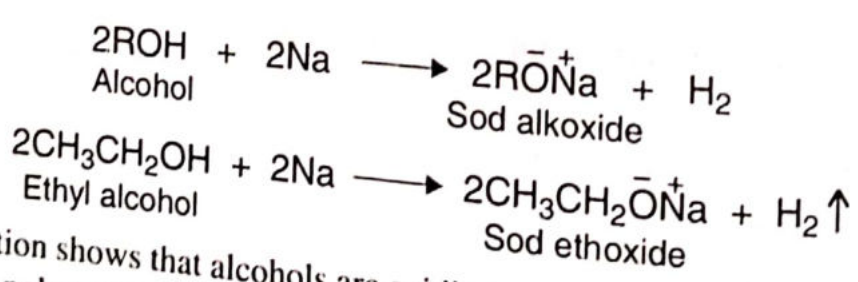


Alcohols undergo the following general reactions :

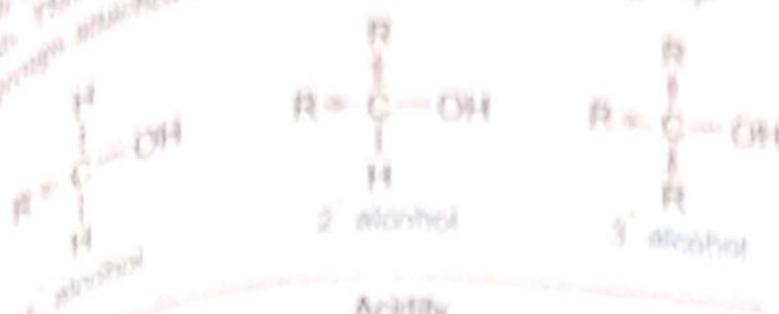


Important reactions of Alcohols

(1) **Reaction with Active Metals.** Alcohols react with sodium or potassium to form alkoxides with the liberation of hydrogen gas.

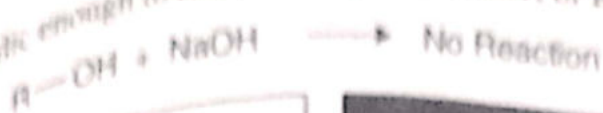


The above reaction shows that alcohols are acidic in nature. The reason for this is that the O-H bond in alcohols is polar and allows the release of the hydrogen atom as proton ( $\text{H}^+$ ). However, alcohols are weaker acids ( $K_a = 10^{-16}$  to  $10^{-18}$ ) than water. This is because the alkyl groups in alcohols



Acidity

Alcohols are not acidic enough to react with aqueous NaOH or KOH.

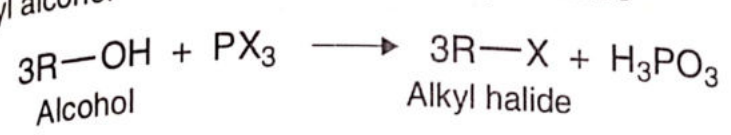
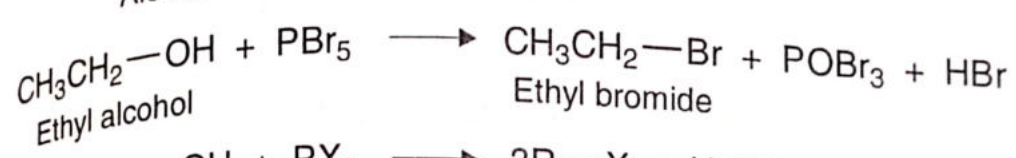
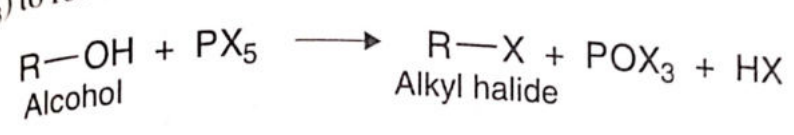


Sodium metal reacts vigorously with alcohols such as methyl alcohol or ethyl alcohol with the evolution of hydrogen gas (Seen as bubbles)



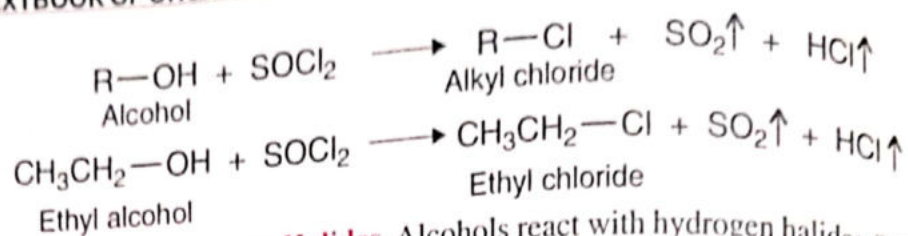
Methyl alcohol has proved to be excellent fuel for racing cars.

**Reaction with Phosphorus Halides.** Alcohols react with phosphorus pentahalides ( $\text{PX}_5$ ) and phosphorus trihalides ( $\text{PX}_3$ ) to form alkyl halides.

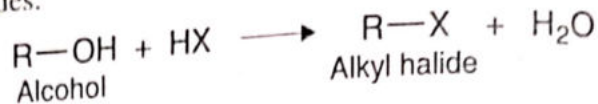


**Reaction with Thionyl Chloride.** Alcohols react with thionyl chloride ( $\text{SOCl}_2$ ) to form alkyl





(4) **Reaction with Hydrogen Halides.** Alcohols react with hydrogen halides (HX) to form corresponding alkyl halides.



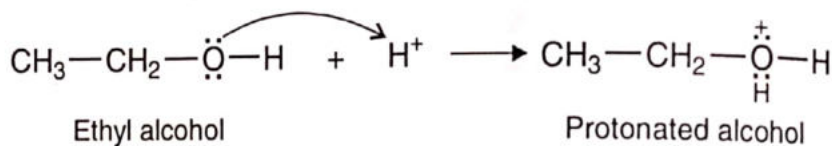
where HX = HI, HBr, HCl



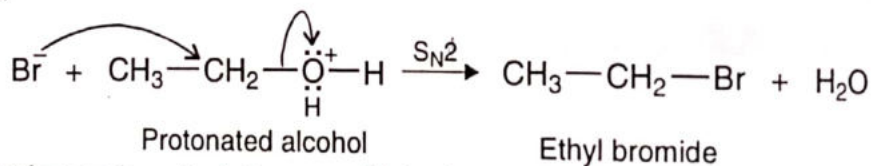
In general, tertiary alcohols react rapidly with hydrogen halides; secondary alcohols react somewhat slower; and primary alcohols, even more slowly. The order of reactivity of hydrogen halides is  $\text{HI} > \text{HBr} > \text{HCl}$ . HCl reacts only in the presence of a catalyst (anhydrous  $\text{ZnCl}_2$ ). No catalyst is required in the case of HBr or HI.

**MECHANISM.** Primary alcohols react with hydrogen halides by an  $\text{S}_{\text{N}}1$  mechanism. The mechanism of the reaction between ethyl alcohol ( $1^\circ$  alcohol) and hydrogen bromide is described below:

**Step 1.** Protonation of ethyl alcohol.



**Step 2.** Nucleophile ( $\text{Br}^-$ ) attacks the carbon holding the protonated hydroxyl group to form ethyl bromide.



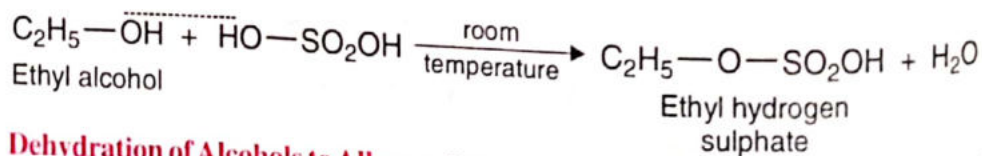
Tertiary and secondary alcohols react with hydrogen halides by an  $\text{S}_{\text{N}}2$  mechanism.

(5) **Reaction with Nitric Acid.** Alcohols react with nitric acid to form alkyl nitrates. For example,

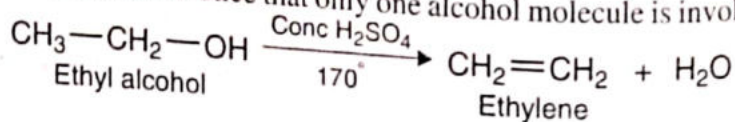


(6) **Reaction with Sulfuric Acid.** The reaction of alcohols with sulfuric acid is very sensitive to reaction conditions. For example,

(i) When ethyl alcohol is treated with concentrated sulfuric acid at room temperature, ethyl hydrogen sulfate is produced.



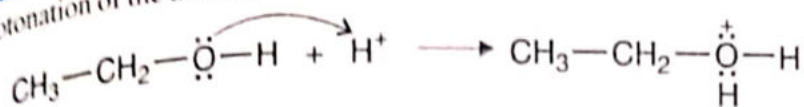
(ii) **Dehydration of Alcohols to Alkenes.** When ethyl alcohol is treated with concentrated sulfuric acid at  $170^\circ\text{C}$ , ethylene is formed. Notice that only one alcohol molecule is involved in the reaction.





**MECHANISM.** The mechanism of the above reaction involves the following steps:

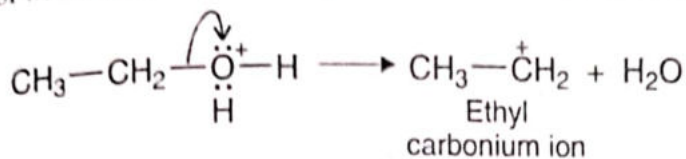
**Step 1.** Protonation of the alcohol molecule.



Ethyl alcohol

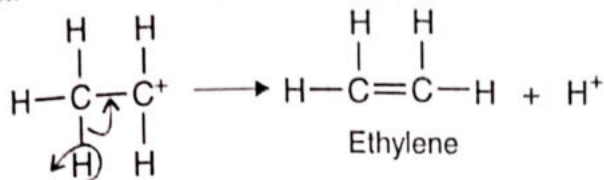
Protonated alcohol

**Step 2.** Elimination of water molecule from the protonated alcohol gives a stable carbonium ion.



Ethyl carbonium ion

**Step 3.** Carbonium ion loses a proton to give the alkene.

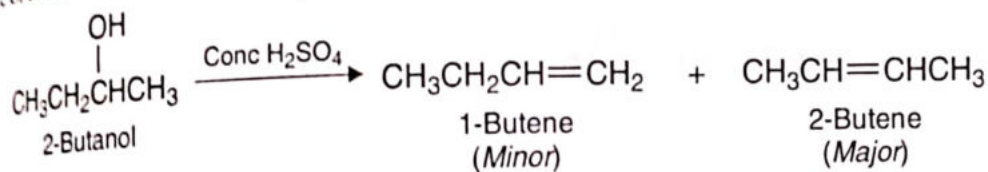


Ethyl carbonium ion

Ethylene

The ease of dehydration of alcohols follows the order  $3^\circ > 2^\circ > 1^\circ$  which is also the order of stability of the carbonium ions.

Dehydration of secondary and tertiary alcohols containing four or more carbon atoms gives a mixture of two alkenes. For example,

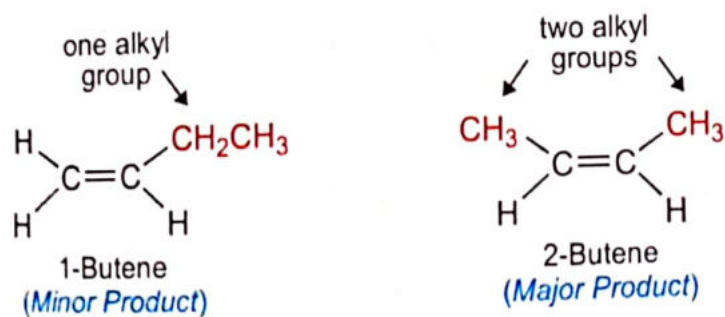


2-Butanol

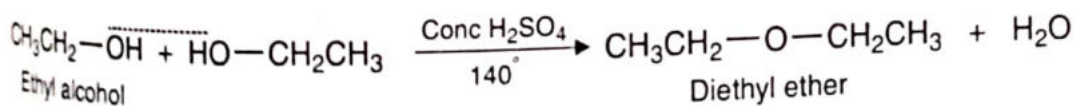
1-Butene  
(Minor)

2-Butene  
(Major)

The alkene produced in greater abundance is indicated by Saytzeff Rule. It states that the alkene formed preferentially is the one containing the higher number of alkyl groups. Therefore, in the above example, 2-butene is the major product.



(iii) **Dehydration of Alcohols to Ethers.** When excess of ethyl alcohol is treated with concentrated sulfuric acid at  $140^\circ\text{C}$ , diethyl ether is formed. Notice that two alcohol molecules are involved in the reaction.

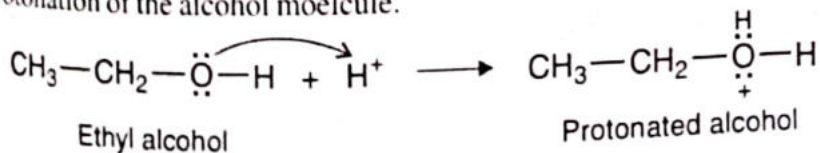


Ethyl alcohol

Diethyl ether

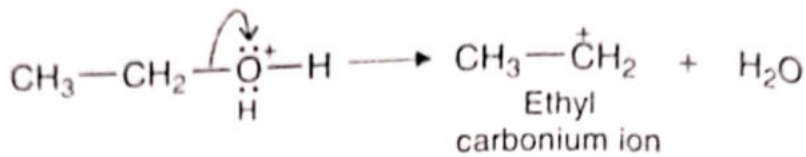
**MECHANISM.** The mechanism of the above reaction involves the following steps:

**Step 1.** Protonation of the alcohol molecule.

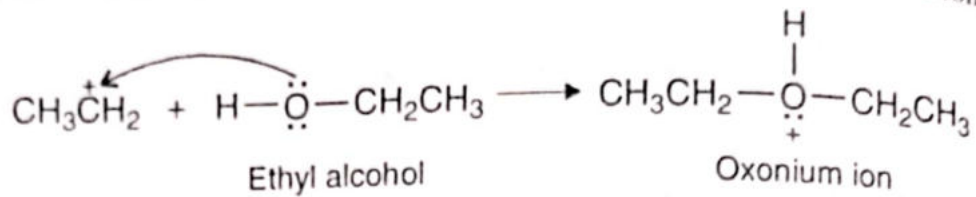


Ethyl alcohol

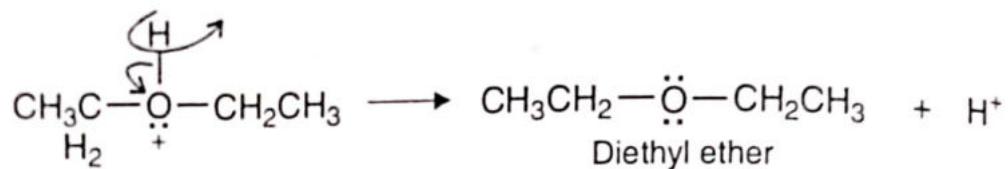
Protonated alcohol



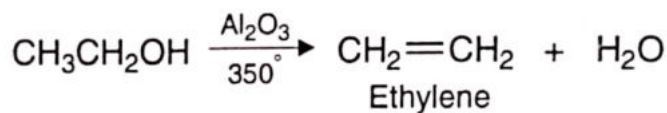
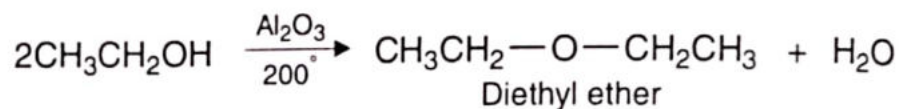
**Step 3.** Carbonium ion attacks another alcohol molecule to form an oxonium ion.



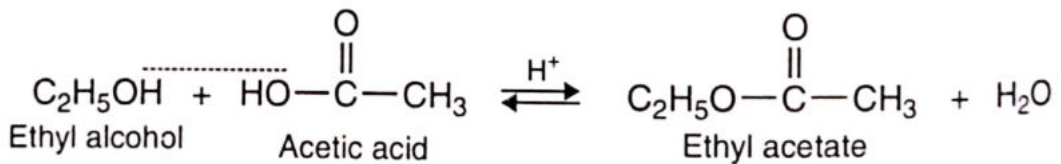
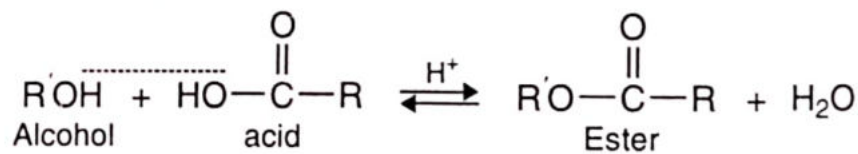
**Step 4.** Oxonium ion loses a proton to form an ether.



Dehydration of alcohols to ethers or alkenes can also be brought about by passing the vapors of the alcohol over heated alumina catalyst. For example,

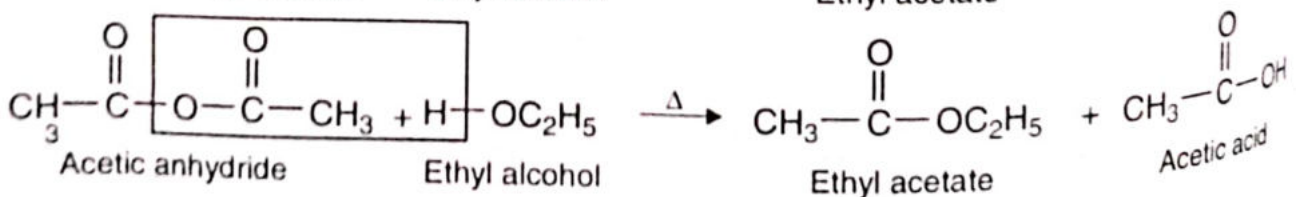
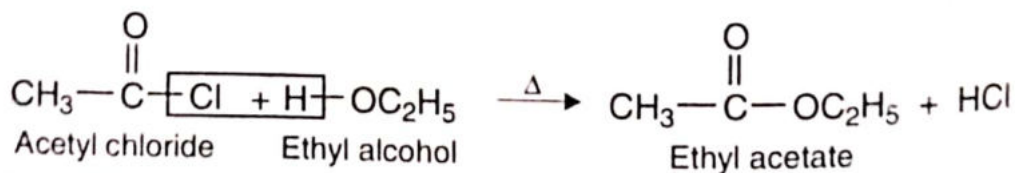


(7) **Reaction with Carboxylic Acids.** Alcohols react with carboxylic acids to form esters. Concentrated sulfuric acid is used as a catalyst. The reaction is reversible and can be shifted in the forward direction by removing water as soon as it is formed.



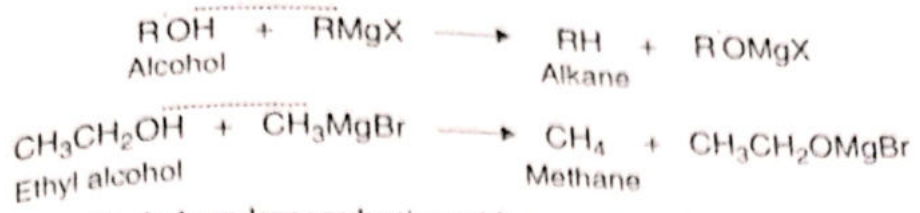
The reaction between an alcohol and a carboxylic acid to form an ester is called **Esterification**.

(8) **Reaction with Acid Halides and Acid Anhydrides.** Alcohols react with acid halides and acid anhydrides to form esters.

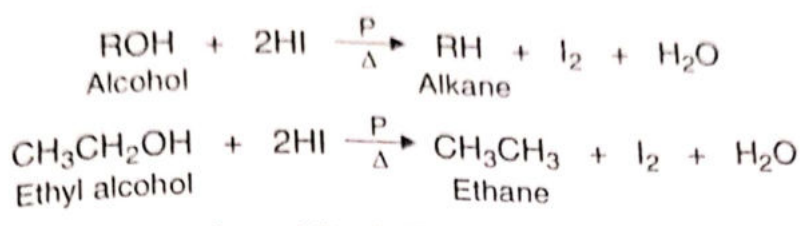




(9) **Reaction with Grignard reagents** Alcohols react with Grignard reagents (RMgX) to form alkanes.

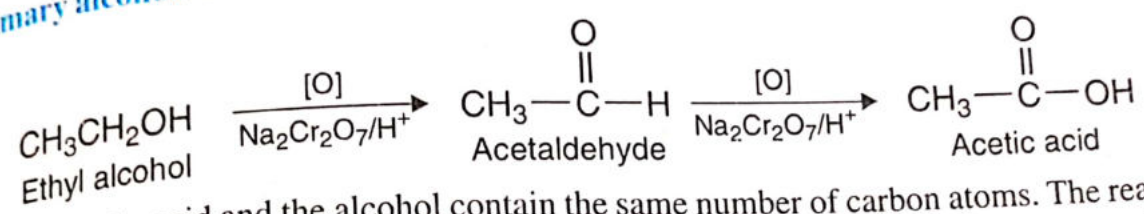


(10) **Reduction** Alcohols undergo reduction with concentrated hydriodic acid and red phosphorus to produce alkanes.



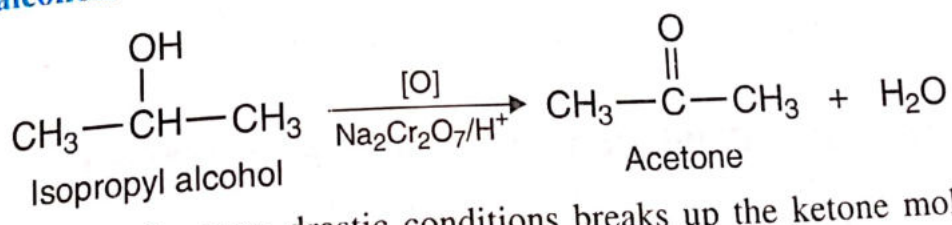
(11) **Oxidation** Alcohols can be oxidized. The nature of the product depends on the type of alcohol and the conditions of the reaction. Most widely used oxidizing agents are  $\text{KMnO}_4 + \text{H}_2\text{SO}_4$  or  $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ . **Oxidation of alcohols can be used to distinguish between primary, secondary, and tertiary alcohols.**

**Primary alcohols** are first oxidized to aldehydes and then to acids.



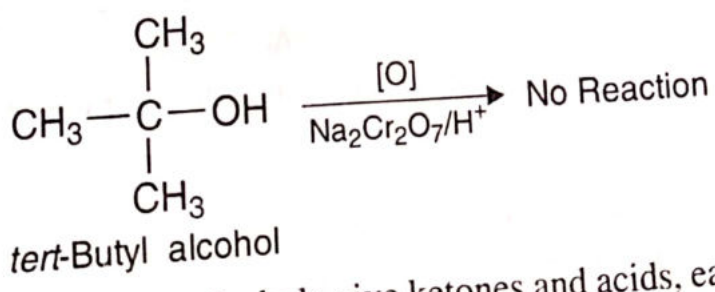
Notice that the acid and the alcohol contain the same number of carbon atoms. The reaction can be stopped at the aldehyde stage by removing it from the oxidizing medium as it is formed (e.g., distillation).

**Secondary alcohols** are oxidized to the corresponding ketones.



Further oxidation under very drastic conditions breaks up the ketone molecule, producing carboxylic acids containing fewer carbon atoms per molecule.

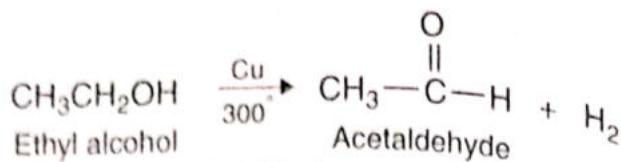
**Tertiary alcohols** are stable to oxidation under normal conditions.



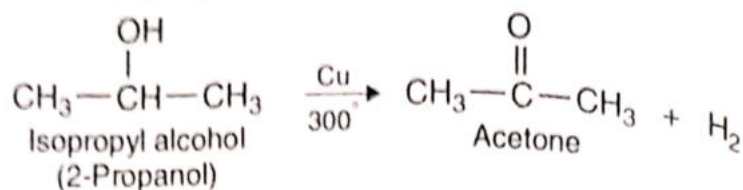
Under drastic conditions, tertiary alcohols give ketones and acids, each containing less than the alcohol.

(12) **Reaction with the Hot Copper ; Dehydrogenation.** Different types of alcohols give products when their vapors are passed over copper gauze at  $300^\circ\text{C}$ .

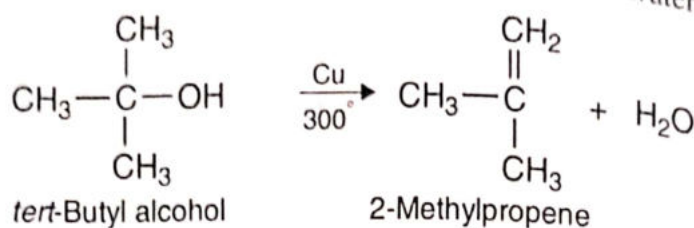
**Primary alcohols** lose hydrogen and give an aldehyde.



**Secondary alcohols** lose hydrogen and yield a ketone.



**Tertiary alcohols** are not dehydrogenated but lose a molecule of water to give alkenes.



### TESTS FOR AN -OH GROUP

The following three 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 the solid compound in an organic solvent such as *dry* ether or benzene.

(1) Add to it small pieces of *Sodium metal*. If bubbles of hydrogen gas are given off, the compound contains an -OH group.



(2) Add to it *Phosphorus pentachloride*. If the mixture becomes warm with evolution of  $\text{HCl}$  gas, the given compound contains an -OH group.

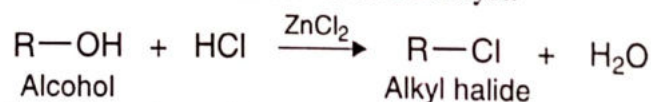


(3) Add *Acetyl chloride* or *Benzoyl chloride* to the substance. The separation of an oily layer, the ester and evolution of  $\text{HCl}$  gas indicates the presence of an -OH group. It may be noted that if the compound was taken in an organic solvent, the oily ester may dissolve in it and thus limiting the test to the evolution of  $\text{HCl}$  gas only.

### HOW TO DISTINGUISH BETWEEN 1°, 2°, AND 3° ALCOHOLS ?

The following tests are used to distinguish between primary, secondary, and tertiary alcohols.

(1) **Lucas Test.** In this test, alcohols are treated with a solution of  $\text{HCl}$  and zinc chloride (*Lucas reagent*) to form alkyl halides. Zinc chloride serves as a catalyst.



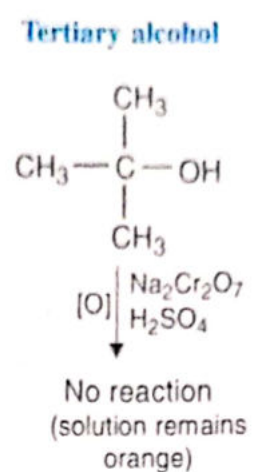
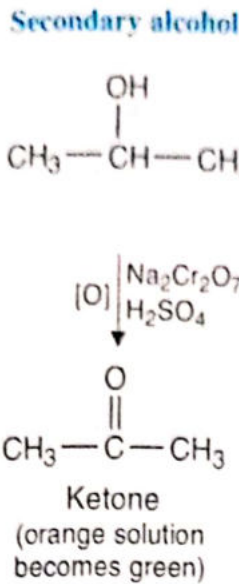
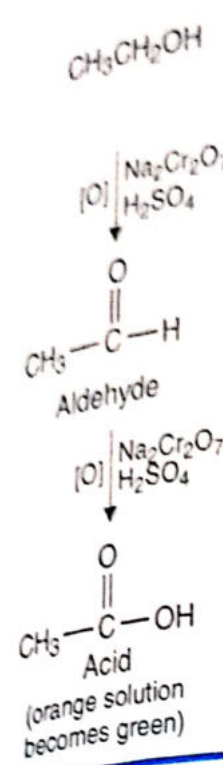
The three types of alcohols undergo this reaction at different rates. Tertiary alcohols react with *Lucas reagent* very rapidly. Secondary alcohols react somewhat slower. Primary alcohols react with *Lucas reagent* even more slowly.

In practice, the *Lucas test* is carried out as follows : An alcohol is mixed, at room temperature, with concentrated  $\text{HCl}$  and  $\text{ZnCl}_2$ . The alkyl chloride, which is formed, is insoluble in the medium. It causes the solution to become cloudy before it separates as a distinct layer.

- With **Tertiary alcohols** cloudiness appears immediately.
- With **Secondary alcohols** cloudiness appears in 5 minutes.
- With **Primary alcohols** the solution remains clear. This is because primary alcohols do not react with *Lucas reagent* at room temperature. High temperatures are needed.



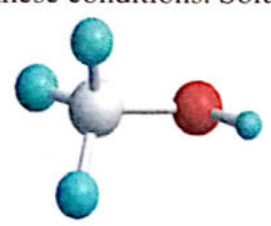
**Table 15.2**  
Primary alcohol



(2) **Dichromate Test.** This test is based on the fact that different types of alcohols give different products on oxidation. The alcohol is treated at room temperature with sodium dichromate in sulfuric acid (orange solution). Identification of the products gives us information regarding the type of the alcohol.

- (a) **Primary alcohols** give a carboxylic acid containing the same number of carbons. There will be a change in color of the solution from orange to green.
- (b) **Secondary alcohols** give a ketone containing the same number of carbons. There will be a change in color of the solution from orange to green.
- (c) **Tertiary alcohols** do not react under these conditions. Solution will remain orange. (Table 15.2)

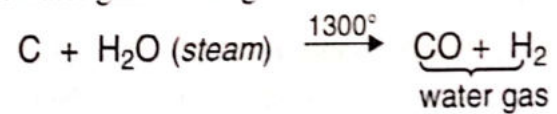
**METHYL ALCOHOL, Methanol, CH<sub>3</sub>OH**



Methyl alcohol is also known as **Wood Alcohol** because it was formerly obtained by the destructive distillation of wood.

**Manufacture.** Methyl alcohol may be prepared by any of the general methods described before. For large scale production, the following three methods can be used :

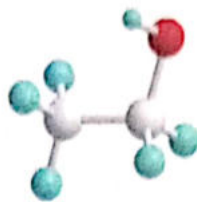
(1) **From Water Gas.** Today, methanol is mostly manufactured by this method. Steam is passed through red-hot coke to form water gas. Water gas is a mixture of carbon monoxide and hydrogen.



Water gas is mixed with half its volume of hydrogen. The mixture is compressed to 300 atmospheres. It is then passed over zinc oxide-chromium oxide catalyst at 300°C. Methyl alcohol vapors are produced which are condensed (Fig. 15.2).

**Uses** Methyl alcohol is used : (1) as a solvent for paints and varnishes ; (2) as an antifreeze for automobile radiators ; (3) to denature ethyl alcohol ; (4) as a motor fuel. A 20% mixture of methyl alcohol and gasoline makes a good motor fuel ; and (5) in the manufacture of formaldehyde.

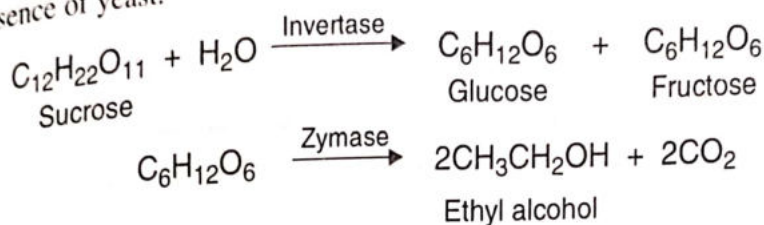
**ETHYL ALCOHOL.** Ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$



Ethyl alcohol is the alcohol of wine, beer, whiskey, and similar beverages. It is often referred to as simply 'alcohol'. Ethyl alcohol is also known as **Grain Alcohol**, since it can be prepared from starchy grains.

**Manufacture.** Ethyl alcohol is manufactured by the following methods :

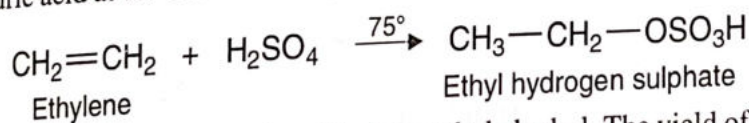
(1) **Fermentation of Sugars.** Ethyl alcohol has been made for centuries by the fermentation of sugars in the presence of yeast.



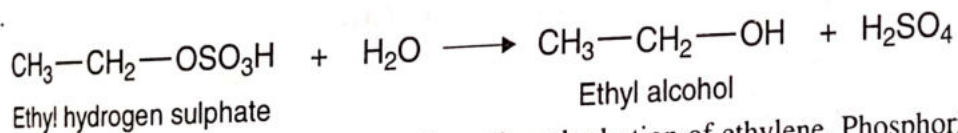
Molasses is a cheap source of glucose, fructose, and sucrose and it forms an excellent raw material for making ethyl alcohol. Ethyl alcohol is also produced from cheap starchy materials such as potatoes, maize and barley. The starchy material is first converted into sugar which is then fermented by yeast.

Just prior to World War II, the fermentation of molasses accounted for about 75% of total world ethanol production. Today less than 10% of ethanol is made by this method. Over 90% is synthesized from ethylene gas which is a by-product of petroleum industry. In India, molasses is still the major source of ethyl alcohol.

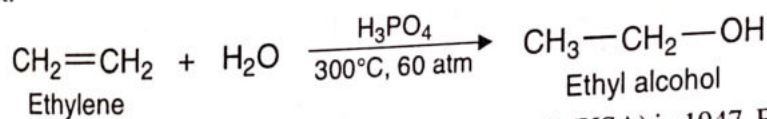
(2) **Sulfuric Acid Process.** This involves indirect hydration of ethylene. Ethylene is treated with concentrated sulfuric acid at  $75^\circ\text{C}$  to form ethyl hydrogen sulfate.



Ethyl hydrogen sulfate is then hydrolysed to form ethyl alcohol. The yield of ethyl alcohol is 90 per cent.



(3) **Phosphoric Acid Process.** This involves direct hydration of ethylene. Phosphoric acid is used as a catalyst.

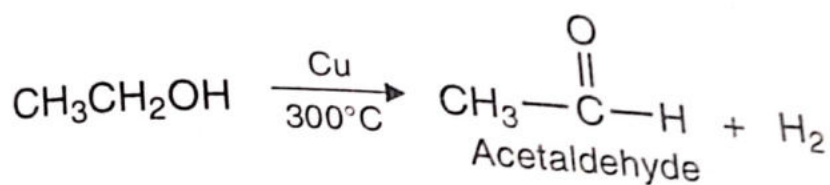


Phosphoric acid process was first used commercially by Shell (USA) in 1947. Ethylene and water are preheated to  $300^\circ\text{C}$  and then passed under high pressure into a reactor. The reactor is a stainless steel vessel containing solid phosphoric acid catalyst. The reaction products are then cooled and passed into the scrubber where ethyl alcohol is dissolved in water. The aqueous solution of alcohol is sent to the distillation tower to get pure alcohol (Fig. 15.3). The yield of ethanol is 95 per cent.

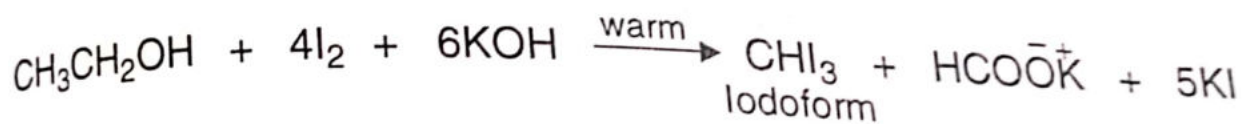


...color extends beyond the yellow centre mark of the tube, the motorist is considered drunk and taken to the police station for further tests.

(13) **Reaction with Hot Copper.** When ethyl alcohol vapors are passed over copper gauze at  $300^{\circ}\text{C}$ , acetaldehyde is formed.



(14) **Formation of Iodoform.** When ethyl alcohol is warmed with aqueous KOH and iodine, iodoform is formed.



**Uses** Ethyl alcohol is used : (1) in the manufacture of alcoholic beverages ; (2) as an industrial solvent ; (3) in the manufacture of drugs, flavoring extracts, and perfumes ; (4) in hospitals as an antiseptic ; (5) as a low freezing (fp  $-114.1^{\circ}\text{C}$ ) and mobile liquid in scientific apparatus such as thermometers and spirit levels ; (6) as an antifreeze in automobile radiators ; (7) in lacquers and varnishes ; (8) as a preservative for biological specimens ; (9) in the manufacture of acetaldehyde, acetic acid, ethyl chloride, and ethyl acetate ; and (10) in the manufacture of synthetic rubber.