

# UNIT 15

## ALCOHOLS |

### Structure

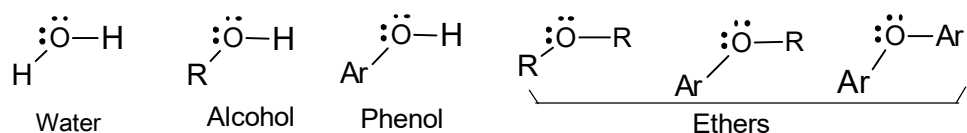
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15.1	Introduction	15.6	Chemical Properties
	Expected Learning Outcomes		Acidic and Basic Nature of Alcohols
15.2	Classification of Alcohols		Reactions of the O-H Bond
15.3	Structure of Alcohols		Reactions of the C-O Bond
15.4	Preparation of Alcohols	15.7	Oxidation of Alcohols
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### 15.1 INTRODUCTION

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In the previous Unit, we described the aryl halides. In this Unit and in subsequent Units, we will discuss oxygen-containing organic compounds. Alcohols and phenols can be regarded as mono-alkyl and mono-aryl substitution products of water, respectively. Similarly, ethers can also be considered as derivative of water in which both the hydrogen atoms of the water molecule have been replaced by alkyl or aryl groups or by both. We shall study the chemistry of phenols and ethers in Unit 16 Unit 17, respectively.



In this unit, we shall take up chemistry of alcohols in detail. Alcohols may also be defined as hydroxy (-OH) derivatives of hydrocarbons. Monohyric alcohols have general formula  $\text{C}_n\text{H}_{2n+1}\text{OH}$ . Alcohols provide us with a great number of useful products, which include germicides, antifreeze agents, pharmaceuticals,

explosives, solvents and plastics. Alcohols also play central role in synthetic organic chemistry. They can be converted into many other types of compounds, including alkenes, alkyl halides, ethers, aldehydes, ketones, and carboxylic acids. These compounds can also be converted back to alcohols.

In this unit, first we will discuss the classification of alcohols, their structure and then give an outline of the different methods available for the preparation of alcohols. We will then review the physical properties of alcohols. Finally, we will consider the chemical properties of alcohols and diols.

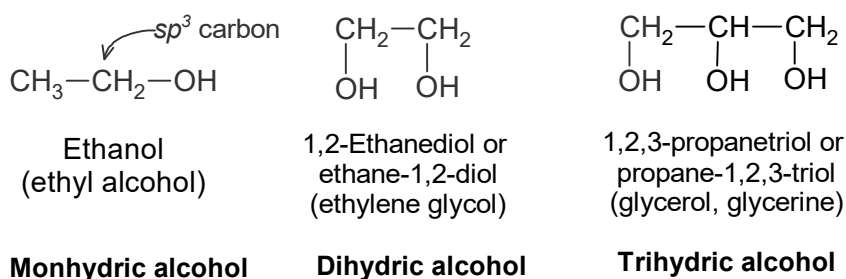
## Expected Learning Outcomes

After studying this unit, you should be able to:

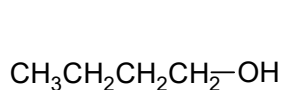
- ❖ classify alcohols;
- ❖ outline the preparation of alcohols;
- ❖ describe the commercial methods for manufacture of alcohols;
- ❖ define the physical properties of alcohols;
- ❖ explain acidic and basic nature of alcohols;
- ❖ describe the reactions of alcohols with active metals such as Li, Na, and K;
- ❖ explain the nucleophilic substitution reactions and acid-catalysed dehydration reactions of alcohols;
- ❖ describe various reagents used for oxidation of alcohols; and
- ❖ explain pinacol-pinacolone rearrangement.

## 15.2 CLASSIFICATION OF ALCOHOLS

Hydrocarbons in which an  $sp^3$  carbon carries a hydroxyl ( $-OH$ ) group are called alcohols. Depending on the number of hydroxyl groups present in the molecule, alcohols are called monohydric (1  $-OH$  group), dihydric (2  $-OH$  groups), trihydric (3  $-OH$  groups) or polyhydric (more than 3  $-OH$  groups).

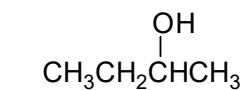


Monohydric alcohols, like the alkyl halides, may be subdivided into primary, secondary and tertiary alcohols. Primary alcohols contain a  $-\text{CH}_2-\text{OH}$  group, secondary alcohols contain the  $\text{R}_2\text{CH}-\text{OH}$  group and tertiary alcohols contain the  $\text{R}_3\text{C}-\text{OH}$  group. For example, the molecular formula  $\text{C}_4\text{H}_9\text{OH}$  can represent the following four monohydric alcohols:



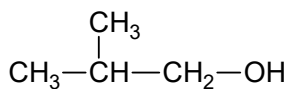
1-Butanol  
(butyl alcohol)

**Primary alcohol**



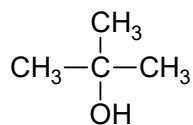
2-Butanol  
(*sec*-butyl alcohol)

**Secondary alcohol**



2-Methyl-1-propanol  
(isobutyl alcohol)

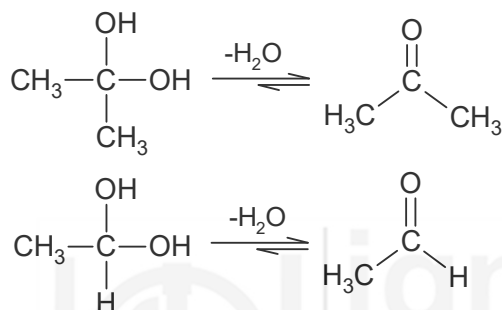
**Primary alcohol**



2-Methyl-2-propanol  
(*tert*-butyl alcohol)

**Tertiary alcohol**

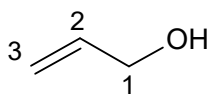
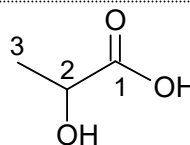
Unlike gem dihalides, gem diols are unstable as they undergo dehydration to the corresponding more stable aldehyde or ketone.



Just to recall, in IUPAC naming of alcohols, the longest chain of carbon containing the hydroxyl group is selected as the parent alkane and numbered from the end closer to hydroxyl group. Finally -e of the parent alkane is replaced with suffix -ol. For naming polyhydric alcohols, the -e of the alkane is retained and suffix -diol (for two hydroxyl groups), triol (for three hydroxyl groups) and so on is added, depending on the number of hydroxyl groups present in a molecule. The common names for alcohols are derived by naming the alkyl group bonded to hydroxyl group and then adding the word alcohol. Common names of several low molecular weight alcohols are still widely used. Therefore, we have used both the common names and the IUPAC names. The common names are given in parentheses below the IUPAC names of the compounds.

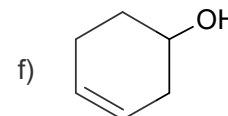
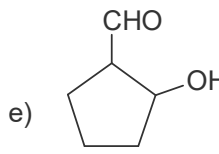
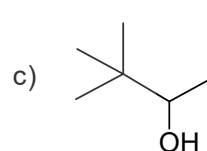
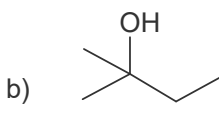
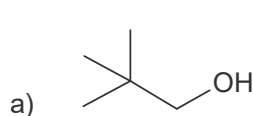
In substituted alcohols, the number for the hydroxyl group is often placed between the infix and suffix. For example, IUPAC name of *tert*-butyl alcohol may be written as 2-methylpropan-2-ol or either 2-methyl-2-propanol, both names are acceptable.

Alcohols with double or triple bonds are named using the -ol suffix on the alkene or alkyne by replacing their -e. In such alcohols, numbering is done in such a way so as to give the hydroxyl group the lowest possible number. When the hydroxyl functional group is present together with a functional group of higher nomenclature priority such as aldehyde, ketone, carboxylic acid derivative or carboxylic acid group, then it must be cited and located by the prefix *hydroxy* and with an appropriate number. For further illustration, some examples are given below.

2-Propen-1-ol  
(allyl alcohol)2-Hydroxypropanoic acid  
(lactic acid)

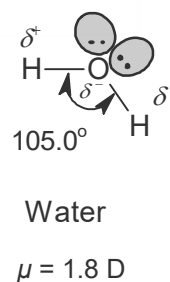
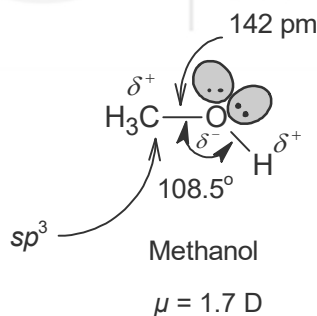
### SAQ 1

Classify each alcohol as primary, secondary or tertiary. Also write IUPAC names of each alcohol.



## 15.3 STRUCTURE OF ALCOHOLS

The Hydroxyl functional group ( $-\text{OH}$ ) of an alcohol is bonded to a  $sp^3$  hybridised carbon. The oxygen atom of an alcohol is also  $sp^3$  hybridised. The two  $sp^3$  hybridised orbitals of oxygen form two  $\sigma$  bonds, one with hydrogen atom and one with carbon atom. Each of the remaining two  $sp^3$  hybridised orbitals of oxygen contain an unshared pair of electrons.



The geometry around oxygen atom of an alcohol molecule is essentially the same as that in water. The measured C-O-H bond angle in methanol is  $108.5^\circ$ , very close to the perfectly tetrahedral angle of  $109.5^\circ$ . Further, both the C-O and the O-H bonds are polar covalent bonds due to the high electronegativity of the oxygen atom. As shown above, in case of methanol molecule, carbon and hydrogen bear partial positive charges and oxygen bears a partial negative charge. The presence of these polar bonds makes alcohols to be polar molecules. The dipole moment ( $\mu$ ) of methanol is very similar to water. You will find, in alcohols their physical and chemical properties are due to these structural aspects i.e. presence of lone pairs of electrons on oxygen and polar bonds (C-O and O-H). We will take up physical and chemical properties after a brief discussion on the preparation of alcohols.

## 15.4 PREPARATION OF ALCOHOLS

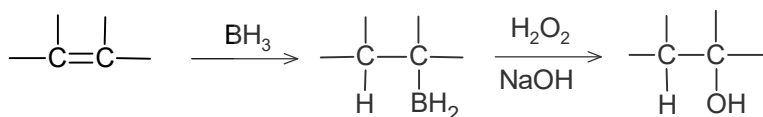
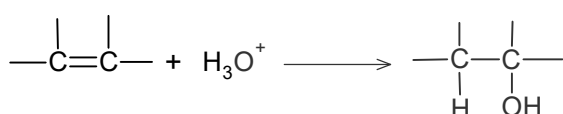
In this section, we will first consider the general methods for the laboratory preparation of alcohols and then take up the industrial preparation of a few important members of this class of compounds.

### 15.4.1 General Methods of the Preparations of Alcohols

Alcohols can be prepared from alkenes, alkyl halides, esters, ethers, aldehydes, ketones and from the Grignard reagents. The general reactions of these methods of preparation are summarised below in Table 15.1.

Table 15.1: Preparation of Alcohols

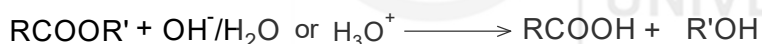
**i) From alkenes**



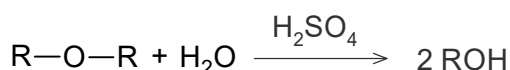
**ii) From alkyl halides**



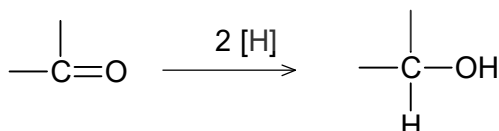
**iii) From esters**



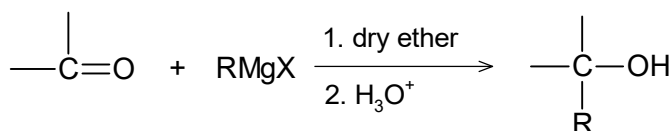
**iv) From ethers**



**v) From aldehydes and Ketones**

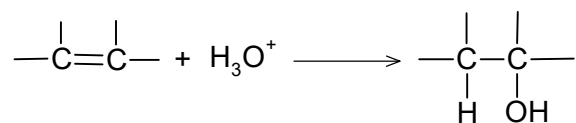


**vi) From Grignard reagent**

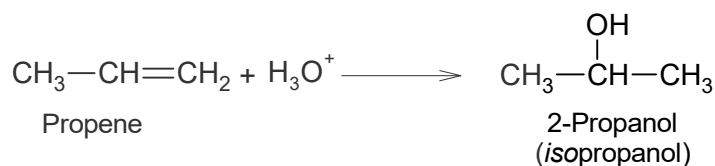


Let us study these methods of preparation in a brief manner.

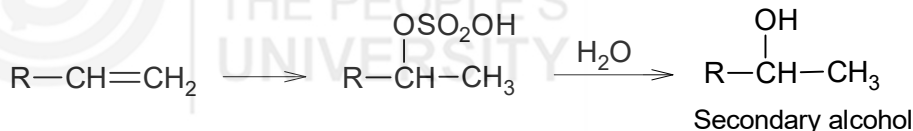
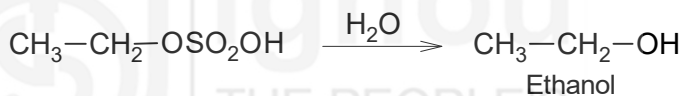
- i) **From Alkenes:** We have already described the acid catalysed hydration of alkenes in Unit 17 of the first Semester chemistry course. In this reaction, the direction of addition is governed by the Markownikoff's rule. The general reaction is,



This method is employed for the preparation of several alcohols:

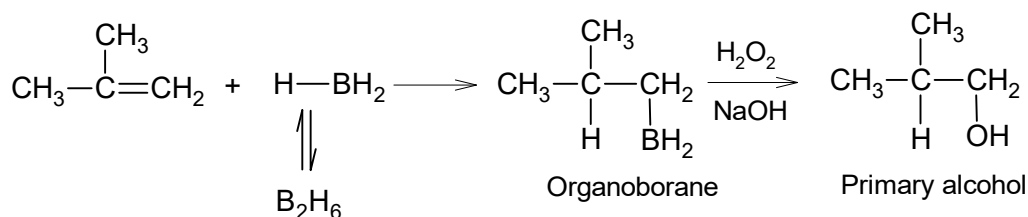


If sulphuric acid is used as the acid catalyst, then the reaction proceeds as follows:

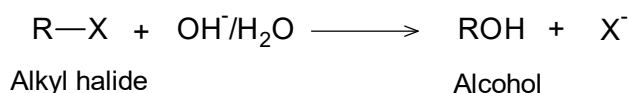


These reactions are useful for laboratory synthesis as well as industrial preparation of alcohols.

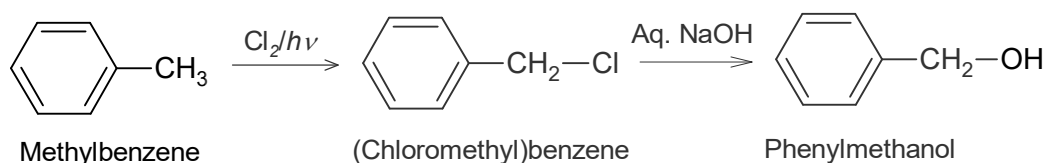
**Hydroboration-oxidation method** is also important because it leads to overall, effective anti-Markownikoff addition of water. We have already described this method earlier in Unit 17 of the first Semester chemistry course. In this method diborane,  $\text{B}_2\text{H}_6$ , is allowed to react with an alkene in an inert solvent such as ether. Diborane is in ready equilibrium with the Lewis acid borane,  $\text{BH}_3$ , which adds to the alkene. Here, the electron seeking (acidic) part of reagent is boron, and addition of  $\text{BH}_3$  proceeds according to Markownikoffs rule to give an intermediate organoborane compound. Oxidation of this intermediate with basic hydrogen peroxide converts it to an alcohol.



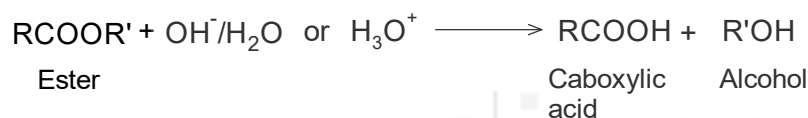
- ii) **From Alkyl Halides:** Hydrolysis of alkyl halides with an aqueous solution of an alkali is a common and convenient method for the synthesis of alcohols, e.g.,



These reactions can proceed *via* S<sub>N</sub>1 or S<sub>N</sub>2 mechanism which we have described in Unit 13. A useful application of this method is in the synthesis of phenylmethanol (benzyl alcohol) from (chloromethyl)benzene (benzyl chloride) which is itself obtained from methylbenzene (toluene) as shown below:

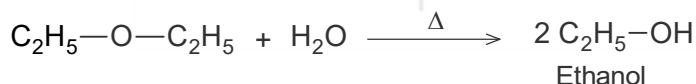


- iii) **From Esters:** Alcohols may be prepared by base or acid catalysed hydrolysis of esters.



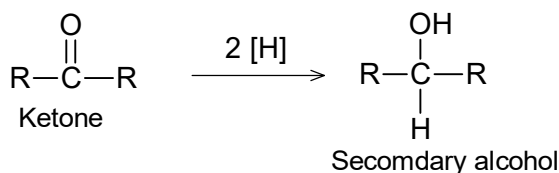
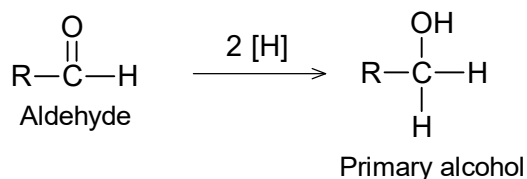
This method is used industrially as certain alcohols occur in nature as esters.

- iv) **From Ethers:** Alcohols are also obtained by heating ethers with dilute sulphuric acid under pressure:

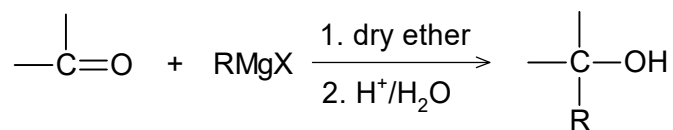


This method is important industrially as the ethers are formed as by-products in the preparation of some alcohols. We will discuss this reaction further in detail in Unit 17.

- v) **From Aldehydes and Ketones:** Alcohols are also obtained by the reduction of aldehydes and ketones with sodium and ethanol or H<sub>2</sub>/Ni or by metal hydrides, such as lithium aluminium hydride. Aldehydes give primary alcohols while ketones secondary alcohols. We will discuss this reaction further in detail in Unit 18.



- vi) **From Grignard Reagents:** Primary, secondary and tertiary alcohols are also prepared by the reaction of suitable carbonyl compound with the Grignard reagent. You have already studied this method in Unit 13.



### SAQ 2

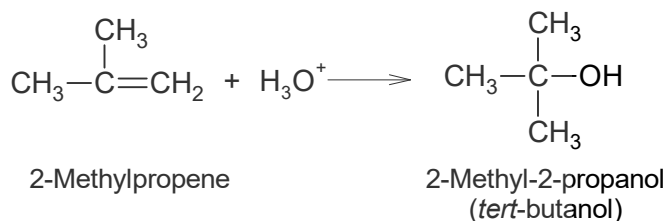
Write chemical equations, showing all necessary reagents, for the preparation of i) 2-butanol and ii) 1-butanol by each of the following methods:

- from an alkene
- from an alkyl halide
- by the Grignard reagent
- by the reduction of ketone/aldehyde.

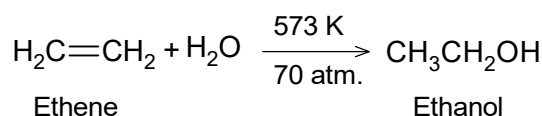
### 15.4.2 Commercial Preparations of Alcohols

Alcohols are of great commercial importance. In this Sub-sec. you will learn how large quantities of these compounds are prepared from different abundant natural sources.

- i) **By the catalytic hydration of alkenes using dilute acid solution:** We have already come across the conversion of alkenes to alcohols in connection with the general methods for small scale preparation of alcohols. The method has been extended to commercial preparations of some alcohols, such as ethanol and 2-propanol. The reactions for the preparation of ethanol and 2-propanol have been already shown. Similarly, hydration of 2-methylpropene (isobutene) in aqueous acidic medium gives *tert*-butanol.

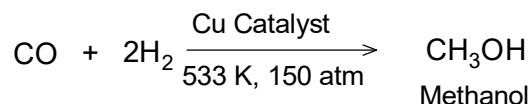


In a recent modification ethene is hydrated directly by passing a mixture of the alkene and steam over a solid acid catalyst (phosphoric acid or silica at 573 K at a pressure of about 70 atmospheres:



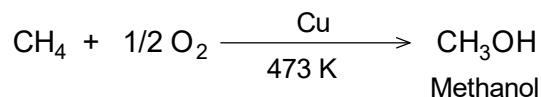
- ii) **By heating a mixture of carbon monoxide and hydrogen under pressure in the presence of a catalyst:** This method is used for the preparation of methanol.





- iii) **By the oxidation of natural gas:** A mixture of methanol, ethanol, propanols and butanols is obtained.

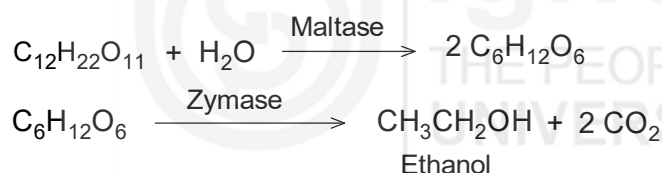
Catalytic oxidation of methane gives methanol:



- iv) **Fermentation of starch:** This method has been the source of ethanol, the constituent of alcoholic beverages responsible for their intoxicating action, since times immemorial. Common sources of starch are wheat, barley, potato, etc. These are mashed with hot water and heated with malt (germinated barley) which contains the enzyme 'diastase'. Enzymatic hydrolysis of starch at 323 K gives the sugar maltose:

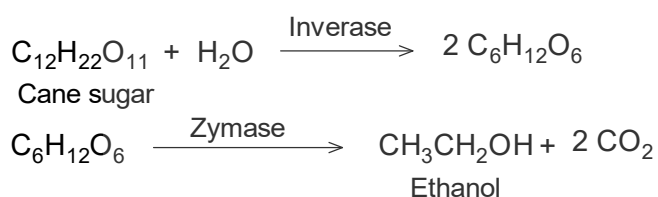


The product is cooled to 303 K and fermented with yeast, which contains various enzymes. One of these, 'maltase', converts maltose to glucose and the other 'zymase' decomposes glucose to ethanol:



Enzymes are a particularly important group of proteins. They are the catalysts which enable living organism to bring about necessary reaction.

Fermentation of molasses (a by-product of sugar industry) also gives ethanol.



Ethanol may also be prepared from glucose directly. Grape juice, a rich source of glucose, ferments to produce wine with a maximum alcoholic content of approximately 12% by volume. The alcoholic content of liquors is usually designated in terms of proof spirit, 100 proof indicating an alcoholic content of about 50% by volume. The term "proof spirit" supposedly has its origin in an early and rather crude analytical procedure for determining the alcoholic content of whisky. Whisky of high alcoholic content, when poured onto the gun powder would ignite and burn with a flame sufficiently hot to ignite the powder also. This was 'proof' of spirit content. If the gunpowder failed to ignite, the presence of too much water was indicated, as the powder would have **become** too wet to burn.

**Absolute ethanol:** Regardless of the methods of manufacture, all aqueous solutions of ethanol on fractional distillation yield a 'constant boiling mixture' of 95 percent ethanol and 5 per cent water which is known as rectified spirit. A constant boiling mixture of two or more liquids, called an azeotrope, cannot be separated by fractional distillation. In order to obtain absolute or 100% pure ethanol, water has to be removed by methods other than fractionation. In the laboratory, rectified spirit is refluxed over quick lime for about 6 hours, and then allowed to stand overnight. On distillation, this gives 99.5 % or lime distilled alcohol. The remaining water is removed by reaction with magnesium metal, by which water is converted into insoluble  $Mg(OH)_2$ .

In industry, calculated amount of benzene is added to the rectified spirit. Distillation of the mixture yields three fractions:

At 338 K, a constant boiling mixture of ethanol, benzene and water (a 'ternary azeotrope').

At 341 K, a constant boiling mixture of ethanol and benzene (a 'binary azeotrope').

At 351 K, pure ethanol or absolute alcohol.

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### SAQ 3

How can the following conversion be carried out on the commercial scale?

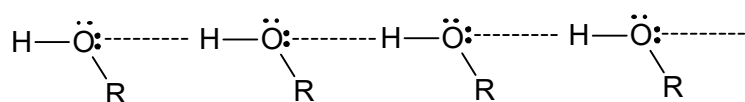
- Ethanol from ethene
  - Methanol from carbon monoxide
  - Ethanol from cane sugar.
- 

## 15.5 PHYSICAL PROPERTIES

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The physical properties of alcohols can be understood if we consider the fact that alcohols are similar in structure to water. As mentioned earlier, the oxygen in an alcohol molecule is in the  $sp^3$  hybridised state and has two unshared pairs of valence electrons. Similar to H–O bonds in water molecules, the C–O and O–H bonds of hydroxyl group of alcohols are polar bonds.

As might be expected, molecules of alcohol like water are strongly hydrogen bonded. The formation of hydrogen bonds leads to the association of a large number of alcohol molecules. These molecular associations have to be broken up before boiling occurs. Hence, alcohols have the higher boiling points when we compared to other molecules of the same size.



Hydrogen bonding in alcohol molecules

Table 15.2 compares the boiling points of some alcohols and chloro compounds with the same carbon skeletons.

**Table 15.2: Comparison of the boiling points of some alcohols and chloroalkanes**

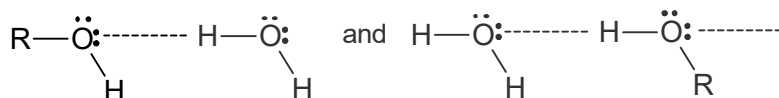
Alcohol	Bp/K	Chloroalkane	Bp/K
CH <sub>3</sub> -OH	337	CH <sub>3</sub> -Cl	249
CH <sub>3</sub> CH <sub>2</sub> -OH	351	CH <sub>3</sub> CH <sub>2</sub> -Cl	286
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> -OH	370	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> -Cl	319

Further, in a group of isomeric alcohols, the primary alcohol has the highest boiling point and the tertiary, the lowest, with the secondary alcohols having an intermediate value. In the straight chain compounds, the van der Waals attractive forces are relatively large due to the large surface area. In the branched chain structures, the molecule tends to become spherical and hence with the decrease in surface area, the attractive forces are also reduced. The physical properties of some alcohols are summarised in Table 15.3.

**Table 15.3: Physical properties of some alcohols**

IUPAC Name	Common name	Formula	Bp/K	Density/ kg dm <sup>-3</sup>	Solubility in water
Methanol	Methyl alcohol	CH <sub>3</sub> O-H	337	0.79	infinite
Ethanol	Ethyl alcohol	CH <sub>3</sub> CH <sub>2</sub> -OH	351	0.79	infinite
1-Propanol	Propyl alcohol	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> -OH	370	0.80	infinite
2-Propanol	Isopropyl alcohol	(CH <sub>3</sub> ) <sub>2</sub> CH-OH	355	0.79	infinite
1-Butanol	Butyl alcohol	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> -OH	380	0.81	8.3 g/100 cm <sup>3</sup>

The water solubility of lower alcohols can also be explained by their ability to form hydrogen bonds with water molecules.

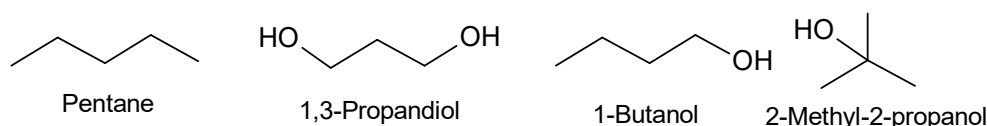


Hydrogen bonding with water molecules

The solubility of alcohols in water decreases as the length of the hydrocarbon chain of the alcohol molecule increases. As discussed in earlier units, the hydrocarbon character of the molecule, i.e., hydrophobic character, increases in higher alcohols.

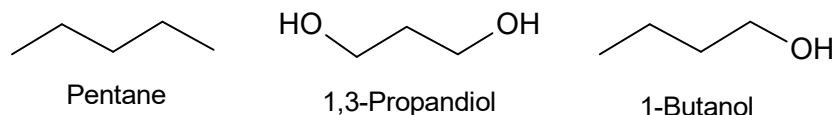
### SAQ 4

Arrange following compounds in order of their increasing boiling points:



## SAQ 5

Arrange following compounds in order of their increasing solubility in water:



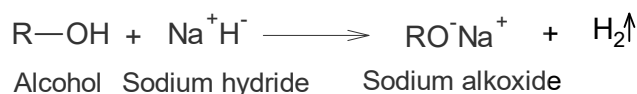
## 15.6 CHEMICAL PROPERTIES

Recall the structure of an alcohol molecule. As mentioned earlier, alcohols have two polar covalent bonds, the C–O bond and the O–H bond. Due to high electronegativity of oxygen both the bonds are polarised so that oxygen is electron rich (nucleophilic) and both carbon and hydrogen are electron deficient (electrophilic). The nucleophilicity of oxygen is further enhanced by the presence of two lone electron pairs on oxygen. You will find that all these structural characteristics will be very useful in predicting the reaction path and mechanism of reactions of alcohols.

The chemical reactions of alcohols involve breaking of either the O–H bond or the C–O bond. In this section, we shall first take up the reactions of O–H bond and C–O bond. Then, we shall look at the oxidation reactions of alcohols. It is observed that many reactions of alcohols are initiated by either accepting a proton or donating a proton. Thus before going in details of these types of reactions of alcohols, let us review acidic and basic properties of alcohols.

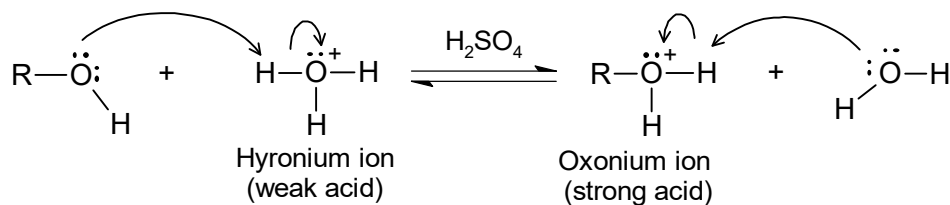
### 15.6.1 Acidic and Basic Nature of Alcohols

Alcohols can function as both weak acids (proton donors) and weak bases (proton acceptors) similar to water. Polar nature of O–H bond is mainly responsible for the acidic behavior of alcohols. Alcohols are much stronger acids than alkanes (by roughly  $10^{30}$  times), and nearly that much stronger than ethers. An alcohol can lose a proton to a strong base yielding an alkoxide ion,  $\text{RO}^-$ . In the reaction given below, alcohol behaves as an acid.



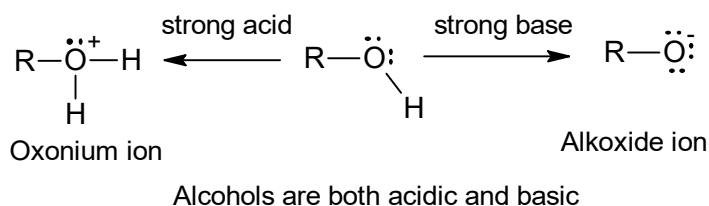
Alkoxides are strong bases, generally stronger than hydroxides. To prepare an alkoxide from an alcohol, we need a base stronger than the alkoxide itself, such as, alkali metal hydrides, NaH, KH, etc.

The oxygen atom of the alcohol molecule has two lone pairs of electrons. These lone pair electrons make alcohols act as a base. For example, in acidic solutions, alcohols are protonated to form oxonium ion. In the reaction given below, alcohol behaves as a base.



Molecules that act both as acids and as bases are called amphoteric (*ampho*, Greek, both). Examples are water, alcohol, etc.

In dilute aqueous solutions, alcohol has approximately the same  $pK_a$  values as water. For example, the  $pK_a$  of methanol in water is 15.5, while that of pure water is 15.74. Therefore, methanol is as acidic as water. Now we can conclude that alcohols are both weak acids and weak base depending on the reaction conditions.



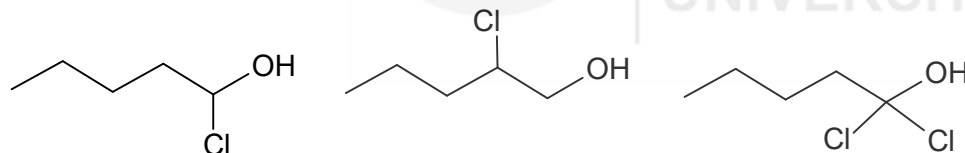
As mentioned above, acidic nature of alcohol is due to the polar nature of the O–H bond. The electron releasing/donating groups such as alkyl group if attached to  $\alpha$ -carbon, increase electron density on oxygen tending to decrease the polarity of O–H bond. This decreases the acid strength of substituted alcohol. Reverse is true with electron attracting/withdrawing group. Electron withdrawing group at  $\alpha$ -carbon, further increases the polarity of O–H bond. The effect of substituents decreases with the distance from the carbon to which O–H group is attached.

We can now write the order of decreasing acid strength.



### SAQ 6

Arrange following alcohols in order of increasing acidity.

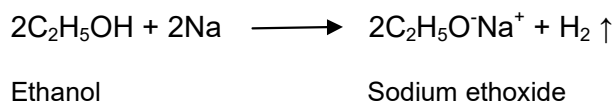


### 15.6.2 Reactions of the O–H Bond

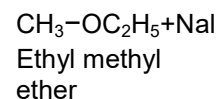
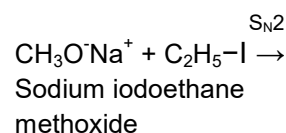
In the previous sub-section, we have seen that with strong base alcohols furnish alkoxides which are valuable both as strong bases and as nucleophiles. Strong acids can protonate alcohols into oxonium ions. This protonation process converts –OH (a poor leaving group) into  $-\text{OH}_2^+$  (a good leaving group) and enabling subsequent nucleophilic substitution or elimination reactions to take place in alcohols similar to alkyl halides. Now, we will take up reactions of alcohols in detail.

#### i) Reaction with Active Metals:

Strongly electropositive metals like K, Na, Mg, Al and Zn liberate hydrogen from alcohols and form alkoxides, e.g.,



The alkoxides of the alkali metals are strong bases (nucleophiles) that enter into  $\text{S}_{\text{N}}2$  substitution of halogen from alkyl halides. This reaction, referred to as the Williamson ether synthesis, is best used to prepare ethers.



In the above reaction, the oxygen-hydrogen bond of the alcohol is broken and the alcohol, thus behaves as an acid. We have mentioned in the previous subsection that alcohols are, however, weaker acids than water. Therefore, the conjugate base of alcohols, the alkoxide ion, is a stronger base than the hydroxide ion, the conjugate base of water. The order of reactivity for different types of alcohols in this reaction is **CH<sub>3</sub>OH > primary > sec. > tert.** This order is the same as given earlier for the acidity of alcohols.

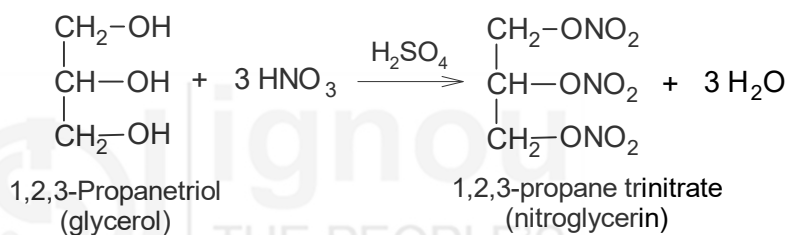
## ii) Esterification:

Another interesting reaction of alcohols is with acids to form esters and water. In this reaction, the oxygen-hydrogen bond in the alcohol is broken.

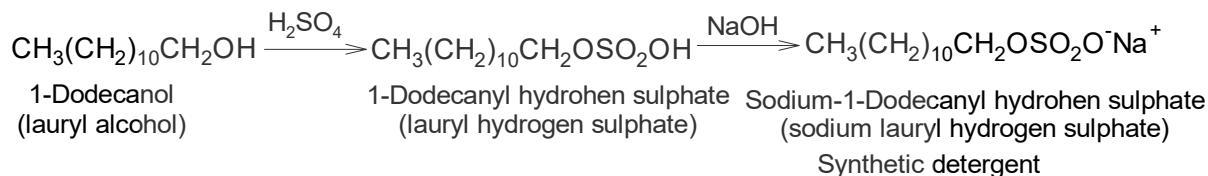


This reaction is known as esterification. These types of reactions will be discussed again in greater detail in the third semester DSC course.

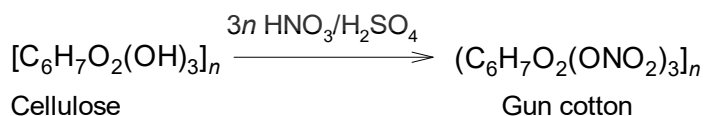
Any inorganic acid can be used in place of carboxylic acid to produce inorganic ester. Inorganic esters are valuable commercial products. For instance, nitroglycerin is readily prepared by the esterification of nitric acid with glycerol.



Nitroglycerin is an explosive used to make dynamite. Similarly, sodium laurylsulphate, a synthetic detergent, can be obtained by esterification of lauryl alcohol,



Another important ester is cellulose trinitrate (gun cotton). It is a product obtained when cellulose (a polysaccharide) is almost completely nitrated under conditions carefully controlled to prevent degradation of the cellulose molecule.

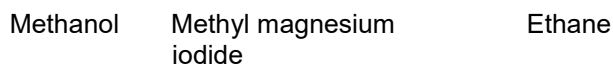
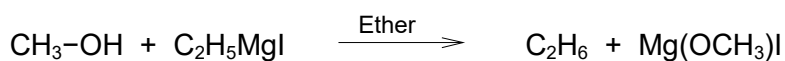
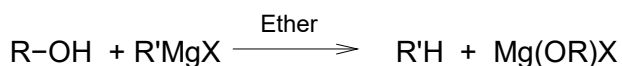


Gun cotton contains about 12-13% of nitrogen, is explosive and is used in the manufacture of smokeless powder.

Esterification of cellulose with acetic anhydride gives cellulose acetate; it is an ester but is not explosive. Cellulose acetate is used to produce thin fibers. From such fiber, the acetate fabrics are woven. Photographic film is also produced from cellulose acetate.

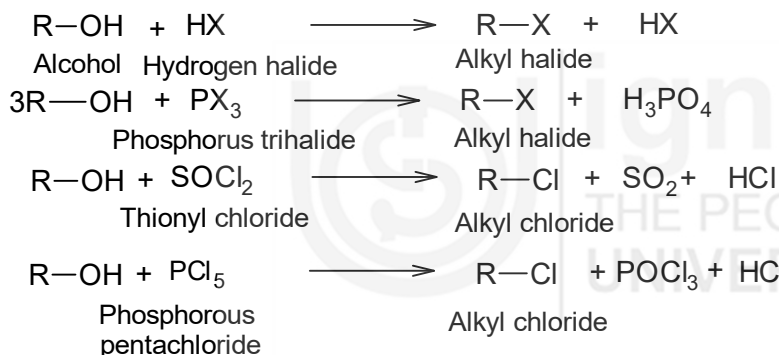
iii) **Reaction with Grignard Regents:**

Alcohols react with Grignard reagents to form alkanes.

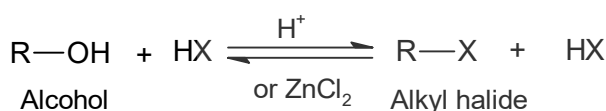
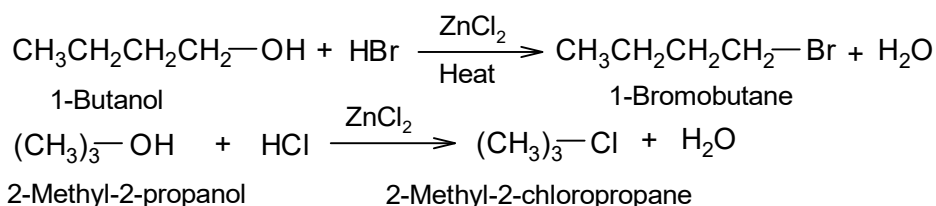
**15.6.3 Reactions of the C-O bond**

We have seen above that the breaking of O-H bond in alcohols is readily achieved with strong bases. We have also mentioned that -OH group (a very poor leaving group) can be changed into a  $-\text{OH}_2^+$  (a better leaving group) by strong acids. Subsequently, C-O may be broken; thereby leading to substitution or elimination reactions. Details of these reactions are as follows.

i) **Substitution Reactions of Alcohols:** The reactions of alcohols with HX,  $\text{PX}_3$ ,  $\text{SOCl}_2$ ,  $\text{PCl}_5$  to prepare alkyl halides have already been briefly discussed in Unit 13.



Let us first look more closely at substitution reaction of alcohol with hydrogen halides (HX). Alcohols can undergo substitution reactions with HX under acidic conditions or in the presence of Lewis acid like anhydrous zinc chloride ( $\text{ZnCl}_2$ ). The general reaction can be represented as,

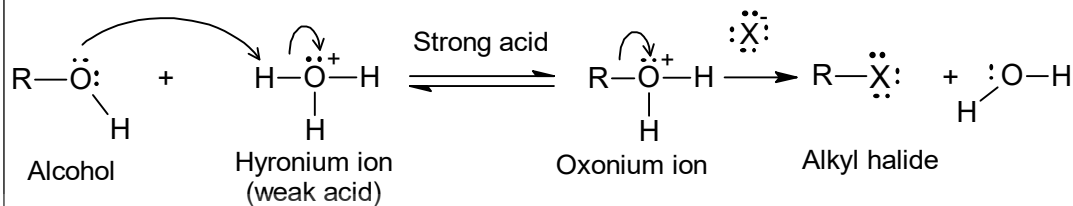
**Example**

If we compare substitution reactions of alcohols and alkyl halides, we can notice that unlike alkyl halides, alcohols do not undergo substitution under neutral or alkaline condition. The reaction requires acidic conditions



A tertiary  $R_3C-OH$  most easily gives a carbocation and tends to react by the  $S_N1$  mechanism. It is very difficult for a primary  $RCH_2-OH$  to form a carbocation, but the primary structure is open to backside attack, so an  $S_N2$  reaction is possible. A secondary alcohol  $R_2CH-OH$  may react by either  $S_N1$  or  $S_N2$  mechanism.

(protonation of  $-OH$  group)) or catalysts like  $ZnCl_2$ . In Unit 13, we have seen that  $Cl^-$ ,  $Br^-$  and  $I^-$  are good leaving-groups and weak bases. But, as you know,  $OH^-$  is a strong base and thus, a very poor leaving group. In acidic solution, alcohols get protonated to  $-OH_2^+$ , which is a good leaving group because it is lost as water, a weak base. A weak nucleophile, such as a halide ion can displace the water molecule to yield an alkyl halide.



The function of zinc chloride is similar to that of proton. Anhydrous zinc chloride is a powerful Lewis-acid with empty orbitals that can accept electrons from the oxygen atom of alcohol. The formation of a complex of  $ZnCl_2$ , with the alcohol oxygen weakens the  $C-O$  bond and thus, enhances the leaving ability of the hydroxyl group.

In substitution reactions of alcohols, the reactivity of the hydrogen halides is as follows:



Thus, the higher the acid strength and nucleophilicity of the halide ion, the higher will be the reactivity towards  $ROH$ .

The order of reactivity of alcohols towards hydrogen halides is as follows:



Increasing reactivity of  $ROH$  towards  $HX$

This order of reactivity forms the basis for the Lucas test which is used to differentiate primary, secondary and tertiary alcohols. The Lucas reagent is made up of concentrated  $HCl$  and  $ZnCl_2$ . Tertiary alcohols react immediately upon shaking with the Lucas reagent to produce an immiscible upper layer of alkyl chloride. Secondary alcohols react in 2-3 minutes, and primary alcohols do not react unless the mixture is heated.

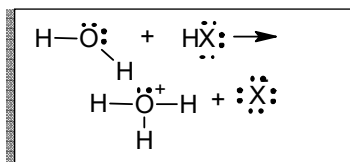
### Mechanism

Like alkyl halides, primary alcohols react by the  $S_N2$  mechanism, tertiary alcohols by  $S_N1$  mechanism, and secondary alcohol by either an  $S_N1$  or  $S_N2$  mechanism.

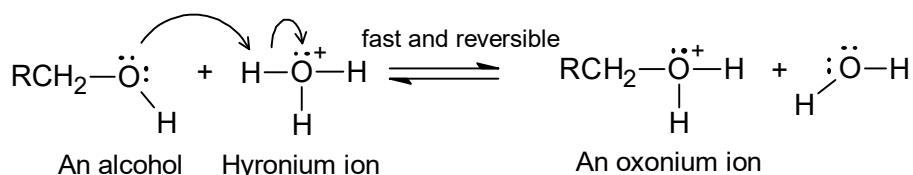
The mechanism for the reaction of primary alcohols is as follows:

#### Step 1

Addition of proton: When an aqueous solution of acid like  $HX$  is used, it forms a hydronium ion. Hydronium ion, actually acts as an acid and transfers proton to  $-OH$  group of an alcohol. The  $-OH$  group of the alcohol gives oxonium ion on accepting proton from hydronium ion. This process converts  $-OH$ , a poor leaving group, into  $-OH_2^+$  which is a good leaving group.

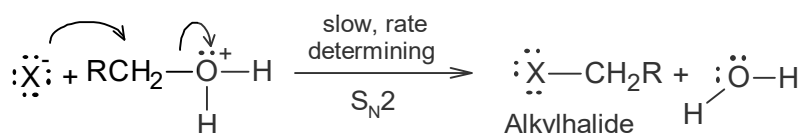






### Step 2

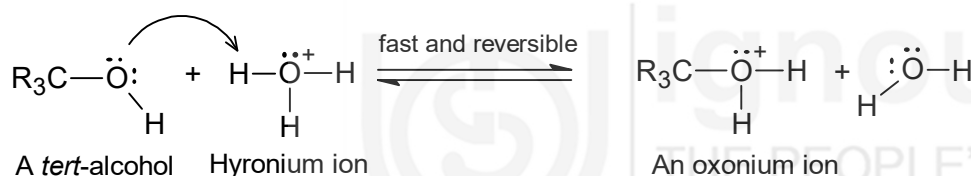
Nucleophile (halide ion) forms new bond with electrophilic carbon centre and simultaneously bond is broken with the leaving group to give stable molecule (an alkyl halide).



The mechanism for the reaction of tertiary alcohols is as follows:

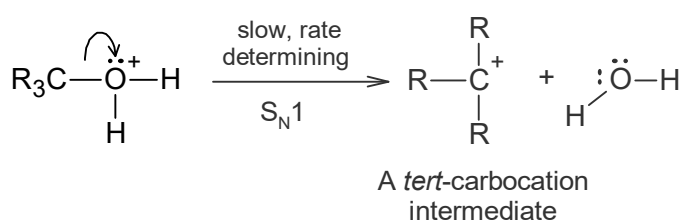
### Step 1

Similar to the first step of the mechanism of the primary alcohol, proton is transferred to convert  $-\text{OH}$  of a *tert*-alcohol, a poor leaving group, into  $-\text{OH}_2^+$ , a good leaving group.



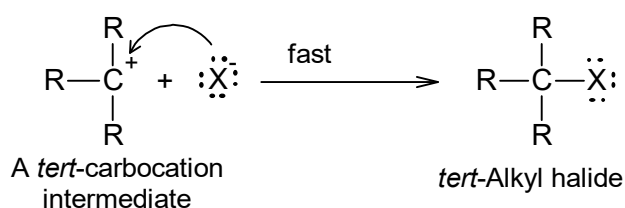
### Step 2

With the loss of water, C-O bond of the alcohol is broken to give a stable carbocation intermediate.



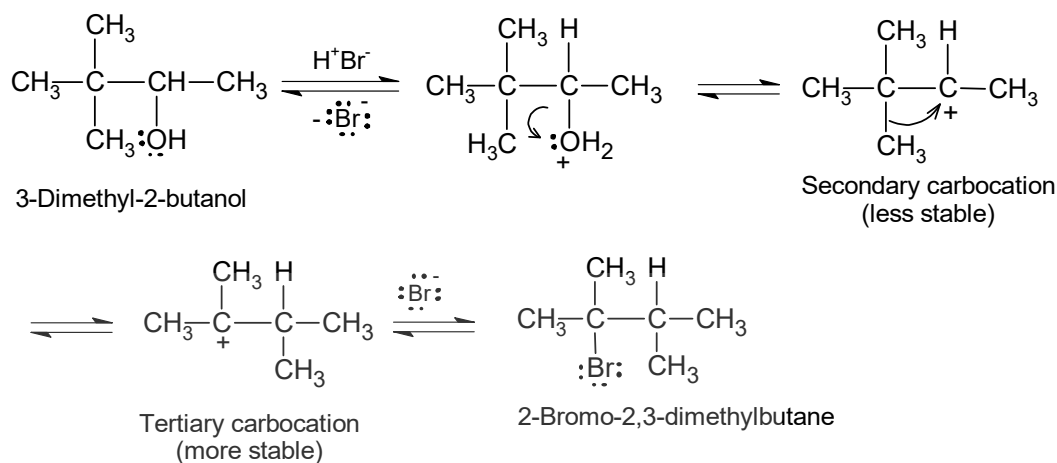
### Step 3

A new bond is formed between electrophilic carbocation and nucleophilic halide ion to form an alkyl halide molecule.



The key feature of nucleophilic substitution reactions with hydrogen halides is conversion of  $-\text{OH}$  group into a good leaving group by the protonation. Such substitution reactions have some limitations. Primary alcohols do not react

with HCl or HF as both chloride and fluoride ions are poor nucleophile in comparison to bromide and iodide ions. Secondary and tertiary alcohols, similar to secondary and tertiary alkyl halides, also tend to undergo rearrangements during the  $S_N1$  reaction.

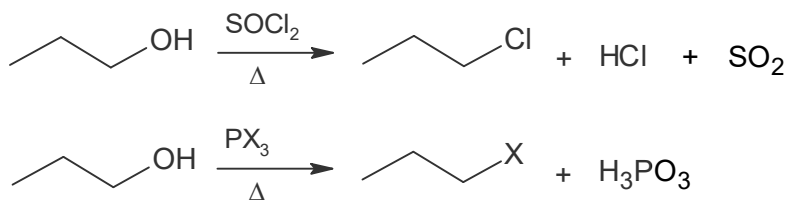


There is also a possibility of protonation of nucleophile in strong acidic conditions unless our nucleophile is a weak acid as our halide ions. Because of all such difficulties, several alternative methods for the preparation of alkyl halides from alcohols have been developed.

Phosphorus and sulphur halides also convert the  $-\text{OH}$  group into a good leaving group and provide a nucleophile, a halide ion, to replace the leaving group.

Most widely used reagents for the conversion of primary and secondary alcohols to alkyl halides are thionyl chloride ( $\text{SOCl}_2$ ) and phosphorus trihalide ( $\text{PX}_3$ ). These reagents undergo reaction under milder reaction conditions with alcohols to form intermediate inorganic esters. The resulting inorganic ester groups are good leaving groups that can be displaced by halide ions.

The reaction with thionyl for conversion of alcohols to alkyl chloride is preferred as by products ( $\text{SO}_2$  and  $\text{HCl}$ ) are gases and are removed from reaction mixture on heating.



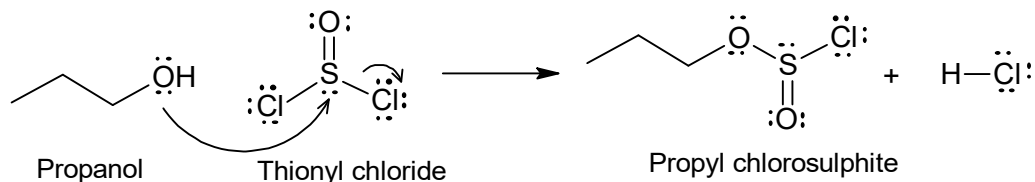
Both these reactions produce good yield of alkyl halides. The mechanisms of these reactions may be written as:

### Mechanism of Reaction with Thionyl Chloride:

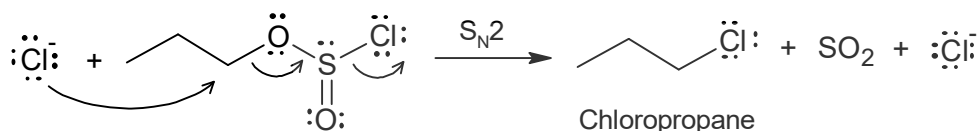
The mechanism of the transformation of the alcohols into corresponding alkyl halides depends on the nature of alcohols. Primary alcohols undergo an  $S_N2$  reaction and tertiary alcohols follow an  $S_N1$  pathway. Secondary alcohols follow both  $S_N1$  and  $S_N2$  pathways.

#### Step 1

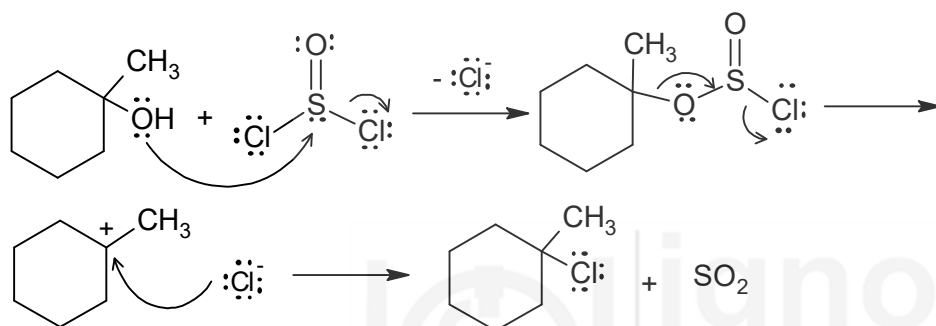
Alcohol reacts with thionyl chloride to form alkyl chlorosulphite, this converts  $-\text{OH}$ , a poor leaving group, into a chlorosulphite that now has a good leaving group.

**Step 2**

In this step nucleophile, i.e. chloride ion displaces leaving group to form the alkyl halide.



Mechanism with *tert*-alcohols



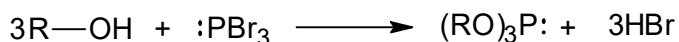
An  $\text{S}_{\text{N}}2$  pathway is favoured in secondary alcohols when a base such as pyridine is added to the reaction mixture.

**Mechanism of Reaction with Phosphorus Trihalides:**

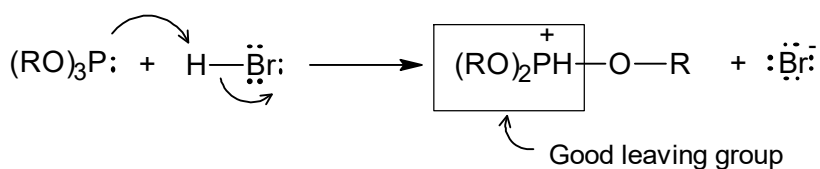
Several phosphorus halides such as  $\text{PCl}_3$ ,  $\text{PBr}_3$  and  $\text{PCl}_5$  are commonly used to convert alcohols to alkyl halides. Amongst them,  $\text{PBr}_3$  is the best reagent for this purpose. Reaction of phosphorus tribromide with primary and secondary alcohols follows  $\text{S}_{\text{N}}2$  pathway. With tertiary alcohols, phosphorus bromide works poorly as in this case back side attack of halide ion on intermediate product (trialkylphosphite) is hindered ( $\text{S}_{\text{N}}2$  condition) and also its ionisation is slow ( $\text{S}_{\text{N}}1$  condition).

**Step 1**

In the first step of the reaction with  $\text{PBr}_3$ , an alcohol forms trialkylphosphite.

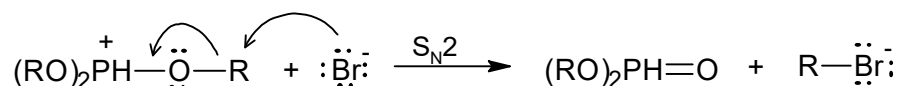
**Step 2**

By extracting a proton from hydrogen bromide, trialkylphosphite forms a good leaving group and generates a nucleophile, bromide ion for next step.



## Step 3

This step leads to substitution with formation of very stable phosphorus-oxygen double bond. This provides the driving force for this step.



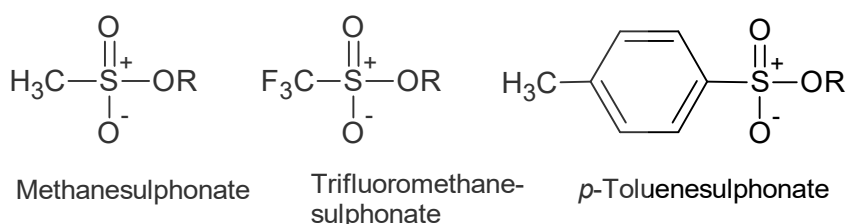
As we have seen that primary, secondary and tertiary alcohols react with different reagents by different pathways. In Table 15.4, we have summarised the best reagent used for the substitution reactions of alcohols leading to alkyl halides.

**Table 15.4: Summary of best reagent used for substitution reactions of alcohols leading to alkyl halides**

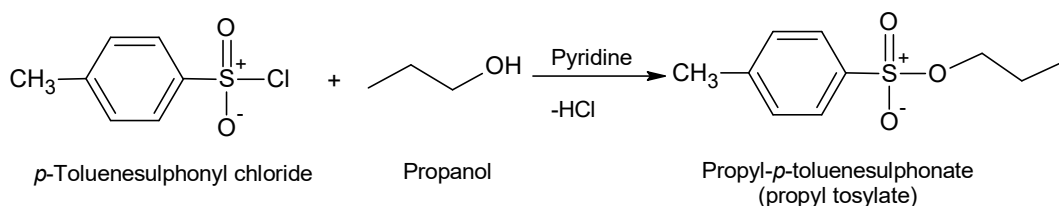
Alcohol	Chloride	Bromide	Iodide
Primary	SOCl <sub>2</sub>	PBr <sub>3</sub>	P/I <sub>2</sub> *
Secondary	SOCl <sub>2</sub>	PBr <sub>3</sub>	P/I <sub>2</sub> *
Tertiary	HCl	HBr	HI

\* Phosphorus triiodide is not a stable compound; therefore, it is generated in the reaction mixture by the reaction of phosphorus with iodine.

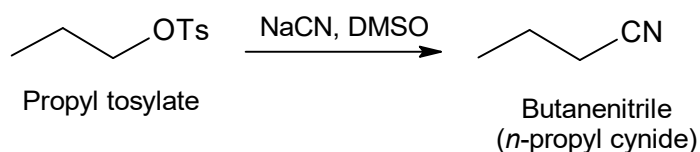
Nucleophiles other than halides also bring about substitution reactions with alcohols. But the –OH group of an alcohol has to be converted into a good leaving group. This is commonly done by converting alcohols into alkyl sulphonate esters. They have very good leaving group, a sulphonate ion. Common sulphonate esters are methanesulphonate (also called mesylate), abbreviated –OMs; trifluoromethanesulphonate (also called triflate), abbreviated –OTf; and *p*-toluenesulphonate (also called tosylate), abbreviated –OTs.



Sulphonates can be prepared by treating an alcohol with alkyl/aryl sulphonyl chloride [for example *p*-toluene sulphonyl chloride (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl or TsCl)] and base which is usually pyridine, triethylamine, or NaOH.

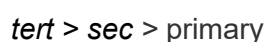


Tosylate (–OTs) being a very good leaving group, can readily be displaced by nucleophile.

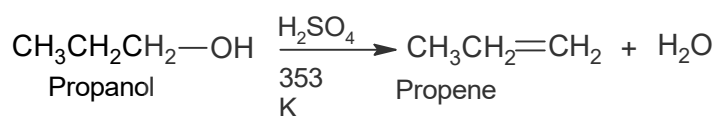


A variety of useful products can be synthesised from alcohols using these two step process.

ii) **Dehydration of Alcohols to Alkenes:** Another reaction of alcohols is the dehydration. This involves cleavage of C–O bond along with loss of a proton from the  $\beta$  position. It may be affected by heating alcohols to 673- 1073 K or heating to a lower temperature in the presence of a catalyst such as alumina or a mineral acid, e.g., sulphuric acid. The product of dehydration of an alcohol is an alkene or a mixture of alkenes. The order of the ease of dehydration of alcohols is:

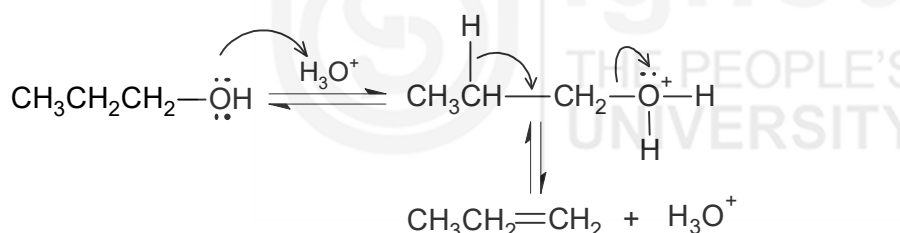


Dehydration of primary alcohols gives only one product, e.g.,

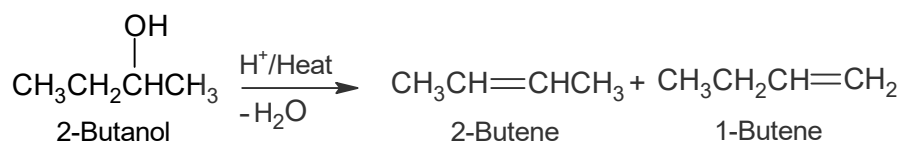


Primary alcohols undergo dehydration reaction by E2 path similar to the dehydrohalogenation mechanism discussed in Unit 13.

For the above reaction the E2 mechanism can be written as,



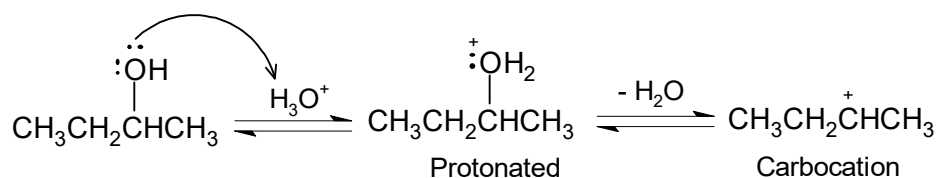
In the case of secondary or tertiary alcohols, a mixture of two alkenes is formed, e.g.,



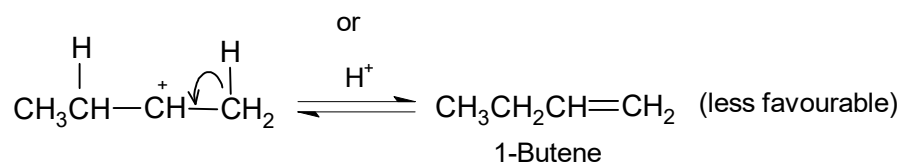
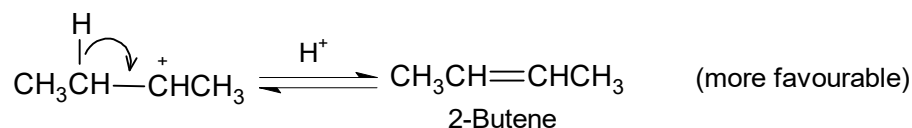
Like the dehydrohalogenation reaction of alkyl halides, the major product in the above reaction is 2-butene, the more substituted alkene (according to Saytzeff rule which was given earlier in Unit 13).

In secondary and tertiary alcohols, dehydration follows the E1 pathway. A detailed discussion of the E1 mechanism has already been given in Unit 13. Now let us write the mechanism for dehydration of 2-butanol.

### Step 1

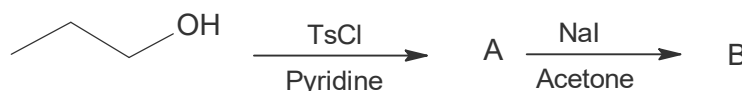


## Step 2



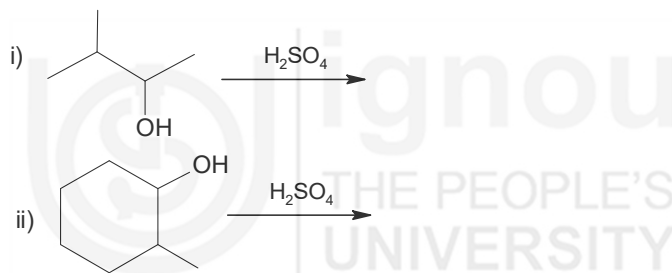
## SAQ 7

Complete the following reaction and write its mechanism:



## SAQ 8

Draw the structure for the alkenes formed in the reactions given below and also predict the major product in each case.



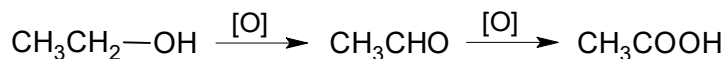
The combination of chromic acid and sulphuric acid is called Jones reagent. This reagent is suitable for the oxidation of secondary alcohols to ketone and primary alcohols to carboxylic acid.

The chromium trioxide complex with pyridine is available in two forms. One is called Collin's reagent: It is prepared by the addition of chromium trioxide to pyridine. The other is Corey's reagent, also called pyridinium chromate complex (PCC), It is made from  $\text{CrO}_3$ ,  $\text{HCl}$  and pyridine. Both these reagents are suitable for the selective oxidation of primary alcohols to aldehydes.

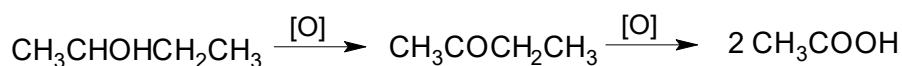
## 15.7 OXIDATION OF ALCOHOLS

Alcohols undergo oxidation and the nature of the product depends on whether the alcohol is primary, secondary or tertiary. The common oxidising agents used are acidic dichromate, acidic or alkaline potassium permanganate or hot concentrated nitric acid or chromic acid ( $\text{H}_2\text{CrO}_4$ ) or the chromium trioxide ( $\text{CrO}_3$ ) complex with pyridine.

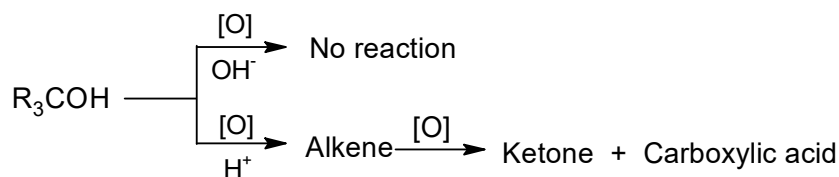
A primary alcohol on oxidation gives an aldehyde, which on further oxidation gives a carboxylic acid. The oxidation products have the same number of carbon atoms as the alcohol, e.g.,



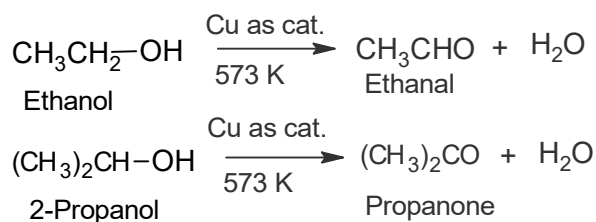
A secondary alcohol on oxidation gives a ketone with the same number of carbon atoms as the alcohol. Ketones are not further easily oxidised. However, drastic oxidations give a mixture of carboxylic acids containing a fewer carbon atoms than the alcohol:



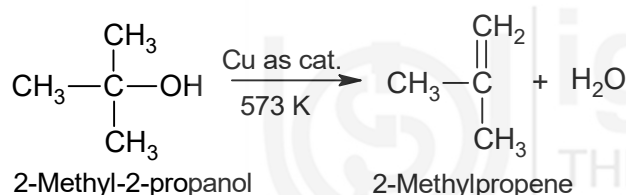
Tertiary alcohols are not easily oxidised in neutral or alkaline conditions. Acidic oxidising agents convert a tertiary alcohol to the alkene and then it is oxidised to a mixture of ketones and carboxylic acids, each having a lesser number of carbon atoms than the alcohol. Oxidation of alkene was discussed in Unit 17 of first semester chemistry course.



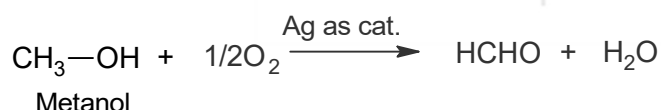
Oxidation of alcohols can also be brought about by catalytic dehydrogenation. In this process, vapours of the alcohol is heated over copper, for example,



As mentioned above, tertiary alcohols are resistant to oxidation. When vapours of tertiary alcohols are passed over copper heated at 573 K, they undergo dehydration to give alkenes, for example,



Silver catalyst is also employed. For example,



Dehydrogenation is more often used for industrial preparation of aldehydes and ketones.

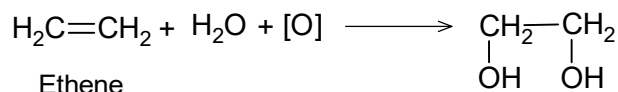
## SAQ 9

Write the product of treating each of the following alcohols with i) PCC, ii) chromic acid.

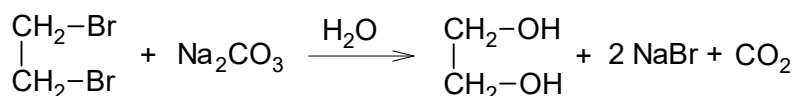
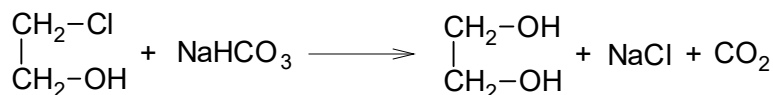
- a) 1-Butanol;    b) 2-Butanol;    c) Cyclopentanol

## 15.8 DIOLS

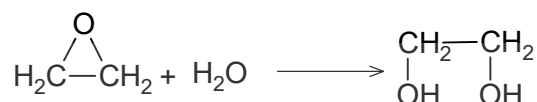
The dihydric alcohols are known as glycols or diols (in IUPAC nomenclature). 1,2-Ethanediol (ethylene glycol or simply glycol) can be prepared by the hydroxylation oxidation of ethene with cold dilute alkaline potassium permanganate:



Hydrolysis of ethene chlorohydrin or 1,2-dihalide with mild alkali, such as aq.  $\text{NaHCO}_3$  or  $\text{Na}_2\text{CO}_3$  also gives 1,2-ethenediol.



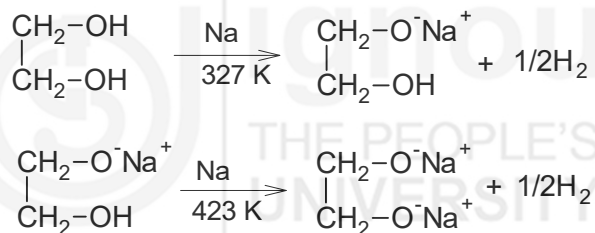
1,2-Ethenediol is manufactured by the hydration of oxirane (ethylene oxide).



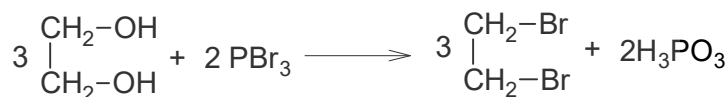
This is carried out in acid solution at about 333 K or with water at 473 K under pressure.

1,2-Ethenediol is taken as a typical example of diols. It shows the chemical reactions of monohydric alcohols except that more vigorous conditions are sometimes needed for reaction of the second of the two hydroxyl groups. For example:

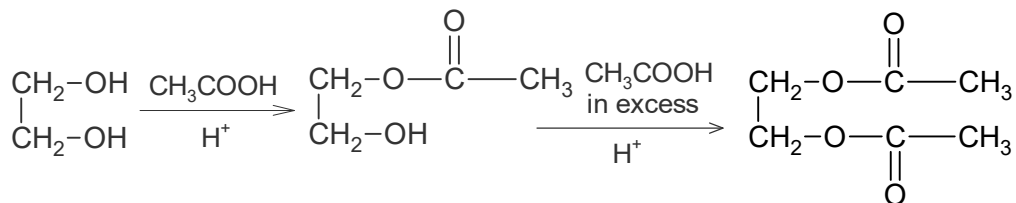
- i) It reacts with sodium to form a monoalkoxide and at higher temperature forms the dialkoxide:



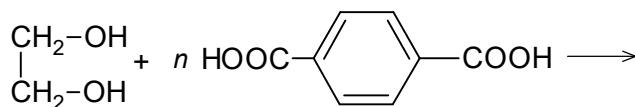
- iii) It reacts with phosphorus halide to yield dihalide:



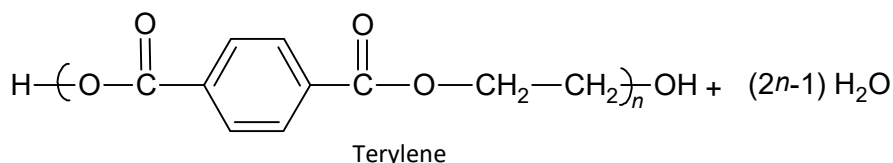
- iv) It reacts with carboxylic acids to form esters:



When esterified with a dibasic acid, it forms polymers, for example,



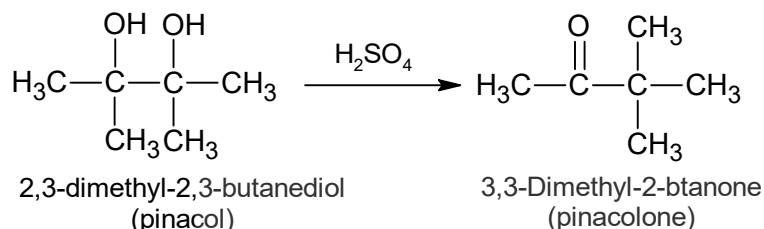
Benzene-1,4-dicarboxylic acid





## v) Acid-catalysed Dehydration of Glycols:

The products of acid-catalysed dehydration of diols are quite different from those of acid catalysed dehydration of alcohols. For example, reaction of 2,3-dimethyl-2,3-butanediol (commonly called pinacol) with concentrated sulphuric acid gives 3,3-dimethyl-2-butanone (commonly called pinacolone).



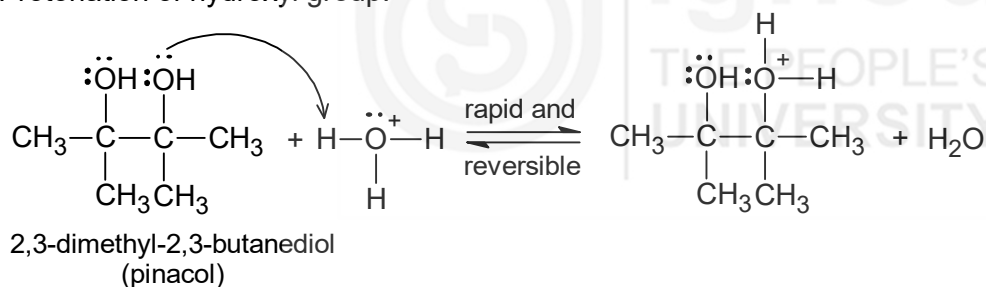
You can notice two important features of this reaction:

- dehydration product is a ketone
- migration of methyl group from one carbon to adjacent carbon

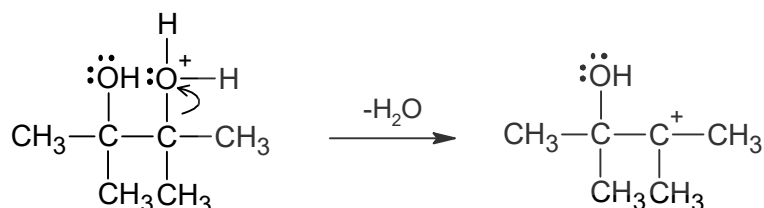
The acid catalysed conversion of pinacol to pinacolone is an example of a rearrangement reaction and called as **Pinacol-pinacolone or simply pinacol rearrangement**. The mechanism of the reaction can be given as shown:

**Step 1**

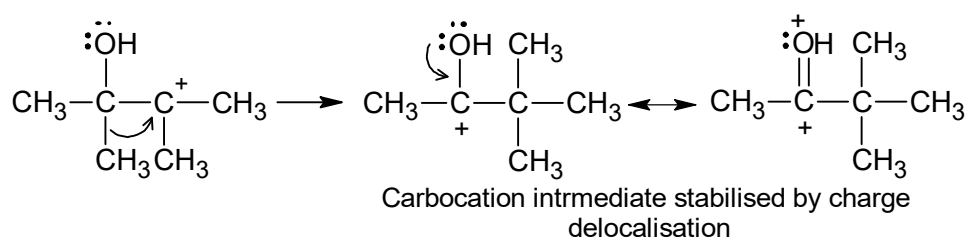
Protonation of hydroxyl group.

**Step 2**

Loss of H<sub>2</sub>O from oxonium ion to form *tert*-carbocation intermediate.

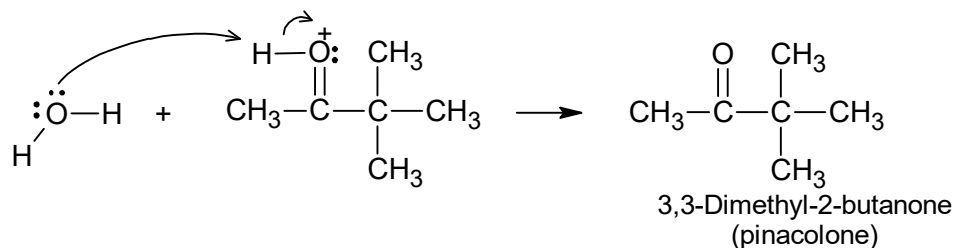
**Step 3**

Migration of methyl group from one carbon to adjacent carbon to form more stable carbocation.

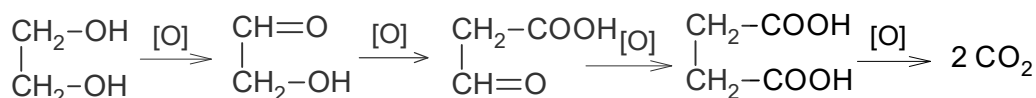


**Step 4**

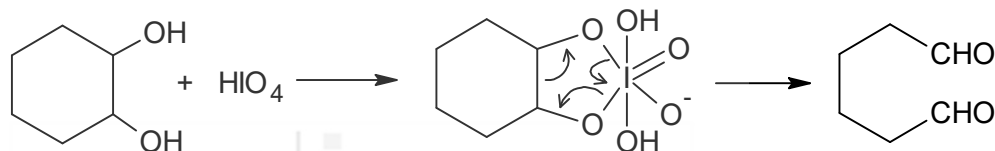
Transfer of proton to solvent



- vi) On oxidation with nitric acid, both the primary alcoholic groups are oxidised, first to aldehyde and then to carboxyl groups. Ethanedioic acid is finally oxidised to carbon dioxide and water,



Oxidising agents such as periodic acid,  $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$  are used for the cleavage of diols, into aldehydes or ketones.

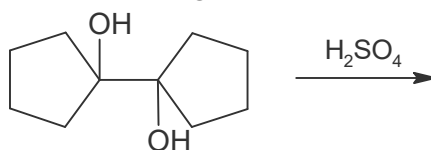


The oxidative cleavage of diols with periodic acid is very useful in the constitutional analysis of sugars.

1-2 Ethanediol is widely used as a solvent, antifreeze agent and in the manufacture of terylene.

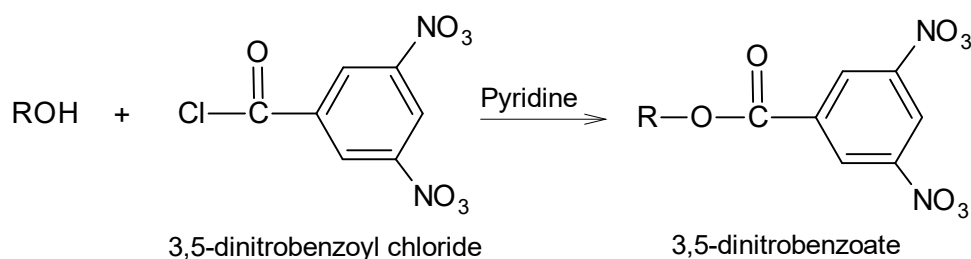
**SAQ 10**

Complete the following reaction:

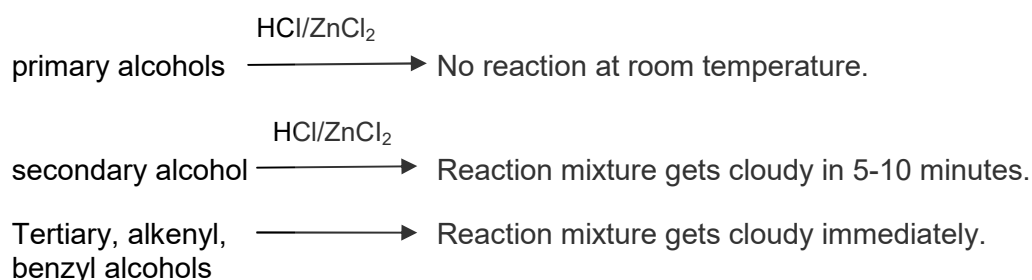
**SAQ 11**What products are formed when 2,3-butanediol is treated with  $\text{HIO}_4$ ?**15.9 LAB DETECTION**

The reaction with sodium metal to evolve hydrogen gas is of some use for the detection of alcohols. The presence of traces of moisture, however, affects the characterisation. The presence of a hydroxyl group in a molecule is often indicated by the formation of an ester upon treatment with an acid chloride or an anhydride. Compounds like alcohols, phenols, primary and secondary amines (those containing an active hydrogen atom) on treatment with benzoyl chloride in the presence of dilute aqueous sodium hydroxide give benzoyl

derivatives (Schotten-Baumann reaction). Sometimes, 4-nitrobenzoyl or 3,5-dinitrobenzoyl chlorides are used to prepare derivatives of alcohols and phenols and thus, for the characterisation of these compounds.



As mentioned earlier, alcohols of different classes can be differentiated on the basis of their reaction rates with HCl/ZnCl<sub>2</sub>. If we take alcohol in a test tube and add mixture of HCl/ZnCl<sub>2</sub> the following results are obtained:



## 15.10 SUMMARY

In this unit, we have described the chemistry of alcohols. We are summarising below what we have studied:

- Alcohols are obtained by the hydrolysis of alkyl halides and reduction of aldehydes and ketones. They are prepared on a large scale by hydration of alkenes, catalytic treatment of water gas, catalytic oxidation of natural gas and fermentation of starch or sugars.
- Alcohols are very weak acids. The molecules tend to associate themselves by forming hydrogen bonds. They react with carboxylic acids to form esters.
- Alcohols can undergo S<sub>N</sub>1 and S<sub>N</sub>2 reaction with hydrogen halides to form alkyl halides. They can also be converted to alkyl halides by the reaction with phosphorous halides and sulphur halides.
- Nucleophiles other than halides also bring about substitution reactions with alcohols. But before that the -OH group of an alcohol has to be converted into a good leaving group. This is commonly done by converting alcohols into alkyl sulphonate esters.
- Dehydration of alcohols leads to alkenes. Oxidation or dehydrogenation of alcohols gives mainly carbonyl compounds.
- Diols undergo pinacol-pinacolone rearrangement reaction under acidic condition.

- Diols can be oxidised by periodic acid to two carbonyl species due to cleavage of the C–C bond between the –OH groups.

## 15.11 TERMINAL QUESTIONS

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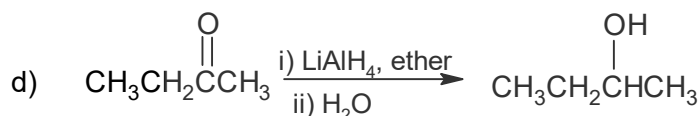
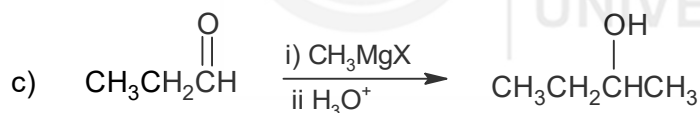
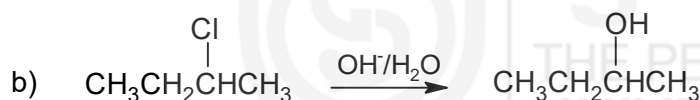
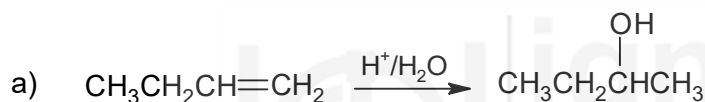
1. Show a structural formula for each name and tell whether it is a primary, secondary or a tertiary alcohol.
  - a) 3-pentanol
  - b) 2,2-dimethyl-1-propanol
  - c) 2-methyl-1-butanol
  - d) 3-methyl-2-pentanol
  - e) 1-methylcyclopentanol
2. Which compound from each pair has a higher boiling point and is more soluble in water.
  - a) 1-chloropropane or propanol
  - b) 1-butanol or 2-methyl-2-propanol
  - c) 2-butanol or 2-propanol
3. Which is the stronger base, ethanol or 2-methyl-2-propanol? Explain.
4. Write the mechanism for the reaction of
  - a) ethyl alcohol with HBr
  - b) 3,3-dimethyl-2-butanol with HBr.
5. Complete the following reactions:
  - a)  $(\text{CH}_3)_3\text{COH} + \text{HCl} \longrightarrow$
  - b)  $\text{C}_2\text{H}_5\text{OH} \xrightarrow[\text{H}_2\text{O}]{\text{Na}}$
6. Show all the alkenes that could possibly be formed by dehydration of each alcohol given below. Which alkene would be produced in largest amount ?
  - a) 2-methyl-2-butanol
  - b) 2-pentanol
  - c) 2-methylcyclohexanol
  - d) 1,2-dimethylcyclohexanol
7. What product, if any, would be obtained by passing each of these alcohols over copper metal at 573 K?
  - a) 1-propanol
  - b) 2-butanol

- c) 2-propanol  
 d) 2-methyl-2-propanol
8. Give a simple chemical test that would distinguish primary alcohol from a secondary alcohol and secondary alcohol from a tertiary alcohol.

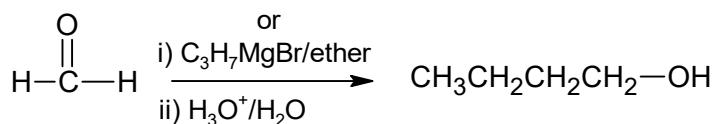
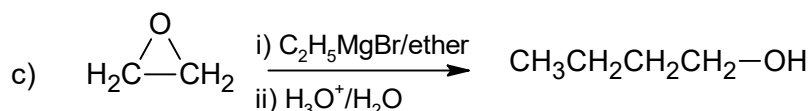
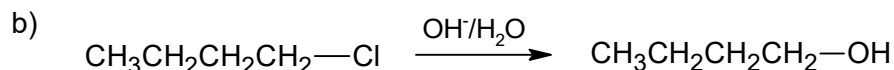
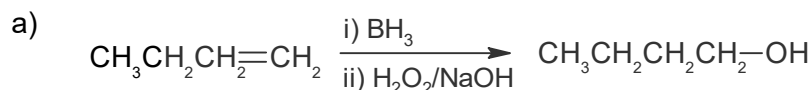
## 15.12 ANSWERS

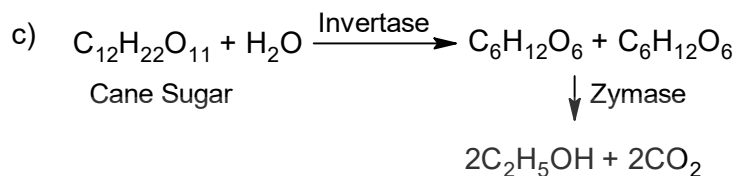
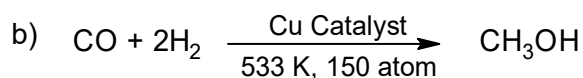
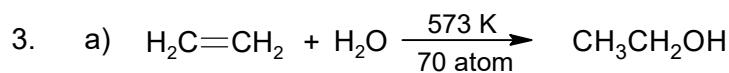
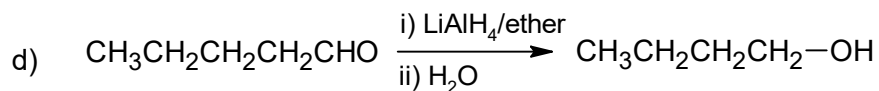
### Self Assessment Questions

1. a) 2,2-Dimethyl-1-propanol or 2,2-Dimethylpropanol, primary  
 b) 2-Methyl-2-butanol, tertiary  
 c) 3,3-Dimethyl-2-butanol, secondary  
 d) 1-Methylcyclohexanol, tertiary  
 e) 2-hydroxycyclopentane-1-carbaldehyde, secondary  
 f) 3-Cyclohexene-1-ol or Cyclohex-3-en-1-ol, secondary
2. i) Preparation of 2-Butanol



- ii) Preparation of 1-Butanol





4. Order of increasing boiling point

Pentane < 2-Methyl-2-propanol < 1-Butanol < 1,3-Propanediol

Explanation: Boiling point mainly depends on two factors:

- (i) The strength of inter molecular hydrogen bonding
- (ii) van der Waals' forces

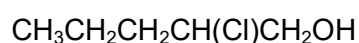
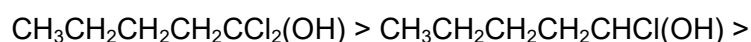
In case of pentane, there is no possibility of hydrogen bonding, therefore, this has the lowest boiling point. 1,3-propanediol has two -OH groups therefore, this alcohol has more sites within its molecule for intermolecular hydrogen bonding than 1-butanol. Now, compare 1-butanol and 2-methyl-2-propanol. Being larger surface area of 1-butanol, this alcohol besides intermolecular hydrogen bonding association has more effective van der Waals forces than 2-methyl-2-propanediol. Thus, 1-butanol has higher boiling point than 2-methyl-2-propanol.

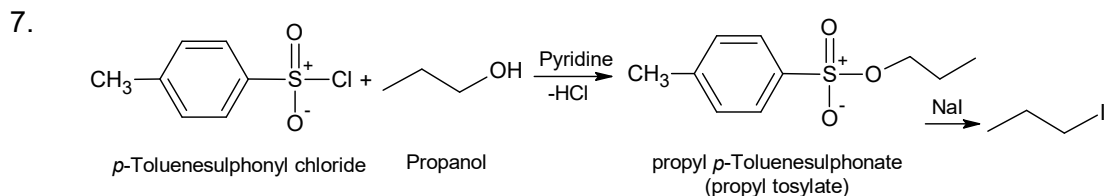
5. Order of increasing solubility in water

Pentane < 1-Butanol < 1,3-Propanediol

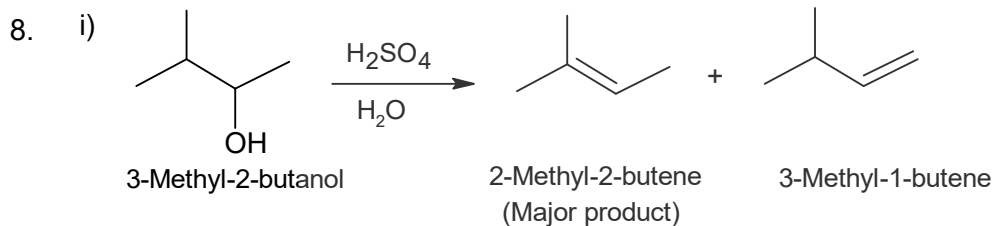
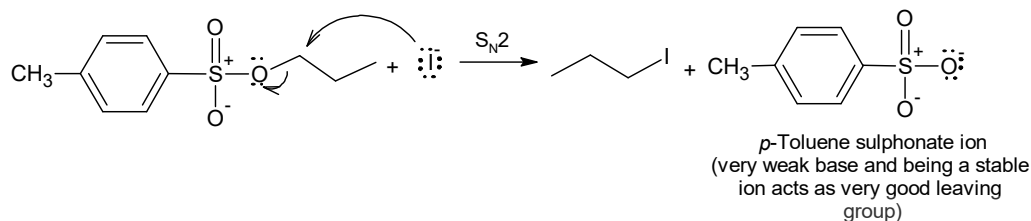
Explanation: Pentane, is a nonpolar molecule, has the lowest solubility in water. Due to the presence of polar -OH group in 1-butanol and 1,3-propanediol, they interact with water molecule by hydrogen bonding. 1,3-propanediol is more soluble in water than 1-butanol as it has more sites within its molecule for hydrogen bonding.

6. Chlorine atom being an electron withdrawing group stabilises the negative charge in the alkoxide oxygen by electron attraction (Inductive effect). Further, such inductive effect increases with the number of electronegative groups on  $\alpha$ -carbon of alcohol but decreases with distance from the oxygen. Thus, on the basis of these facts, the order of acidity will be

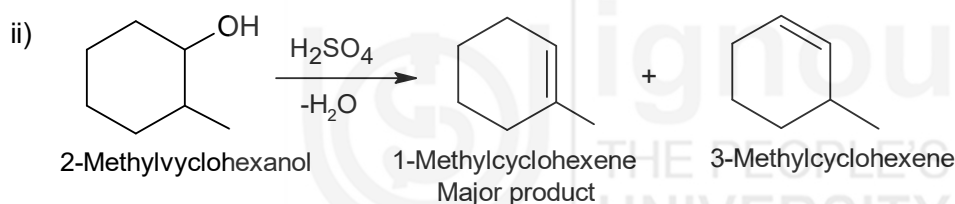




Mechanism

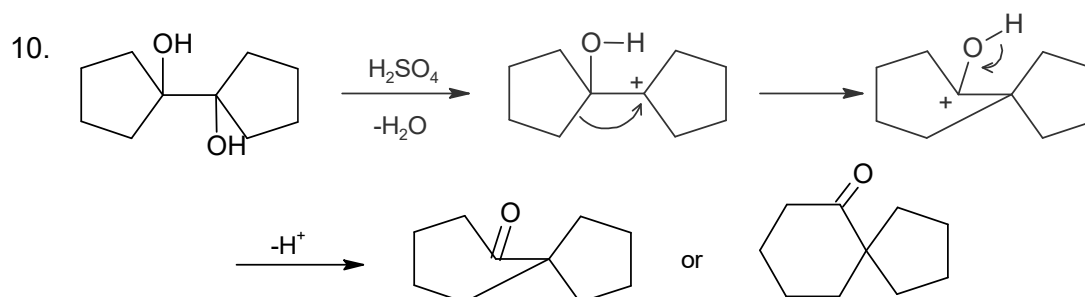


2-Methyl-2-butene has three alkyl groups (methyl groups) on the double bond and 3-methyl-1-butene has only one substituent; thus, former will be the major product as per the Saytzafev rule i.e. formation of more substituted alkene is favoured.

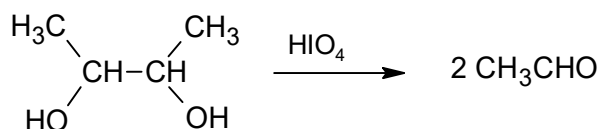


1-Methylcyclohexene has three alkyl substituents on the double bond and 3-methylcyclohexene has two, therefore, 1-Methylcyclohexene will be the major product.

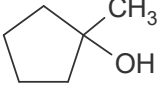
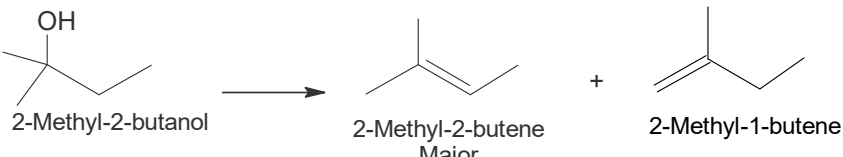
9. 1-Butanol, a primary alcohol, is oxidised to butanal with PCC and to butanoic acid with chromic acid. On the other hand 2-butanol is a secondary alcohol oxidised to butanone by both PCC and chromic acid. Cyclopentanol is also secondary alcohol; it is oxidised to cyclopentanone by both oxidising agents.

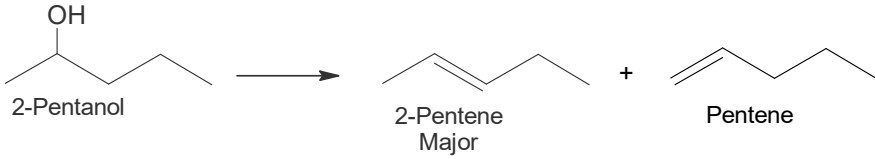


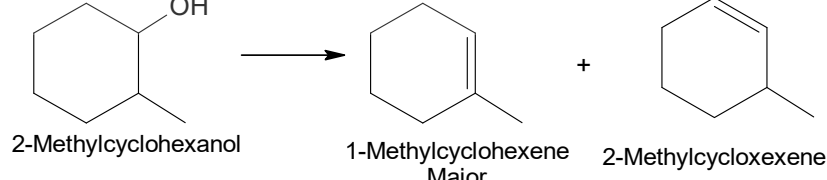
11. The bond between the carbons bearing  $\text{-OH}$  group is cleaved and each  $\text{-OH}$  is converted to a carbonyl group.

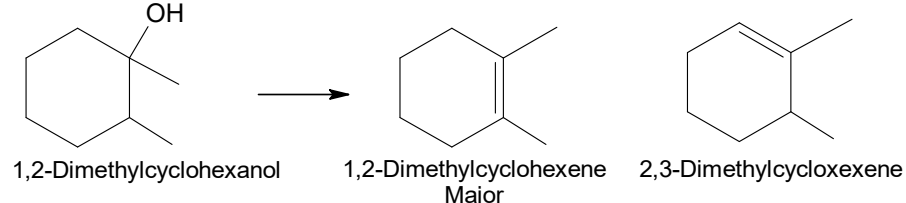


### Terminal Questions

- $$\text{CH}_3\text{CH}_2\overset{\text{OH}}{\text{CH}}\text{CH}_2\text{CH}_3$$
 (secondary)
  - $$\text{CH}_3\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{CH}_2\text{OH}$$
 (Primary)
  - $$\text{CH}_3\text{CH}_2\overset{\text{CH}_3}{\text{CH}}\text{CH}_2\text{OH}$$
 (Primary)
  - $$\text{CH}_3\text{CH}_2\overset{\text{CH}_3}{\underset{\text{OH}}{\text{CH}}}\text{CH}_3$$
 (secondary)
  -  (tertiary)
- |                     |             |              |              |
|---------------------|-------------|--------------|--------------|
| Boiling point       | a) propanol | b) 1-butanol | c) 2-butanol |
| Solubility in water | a) propanol | b) 1-butanol | c) 2-butanol |
- 2-Methyl-2-propanol is less acidic and more basic as it has two electron releasing methyl groups at  $\alpha$ -carbon.
- See Subsec. 15.6.2.
- $$(\text{CH}_3)_3\text{COH} + \text{HCl} \longrightarrow (\text{CH}_3)_3\text{CCl} + \text{H}_2\text{O}$$
  - $$\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{Na}} \text{C}_2\text{H}_5\text{ONa} + 1/2 \text{H}_2$$
- 

2-Methyl-2-butanol  $\longrightarrow$  2-Methyl-2-butene Major + 2-Methyl-1-butene
  - 

2-Pentanol  $\longrightarrow$  2-Pentene Major + Pentene
  - 

2-Methylcyclohexanol  $\longrightarrow$  1-Methylcyclohexene Major + 2-Methylcyclohexene
  - 

1,2-Dimethylcyclohexanol  $\longrightarrow$  1,2-Dimethylcyclohexene Major + 2,3-Dimethylcyclohexene



7. a) 1-propanal, b) 2-butanone  
c) Propanone, d) 2-methylbutene
8. Lucas reagent ( $\text{HCl}/\text{ZnCl}_2$ ) is used to differentiate primary, secondary and tertiary alcohols. Tertiary alcohols react immediately upon shaking with Lucas reagent in a test tube. Secondary alcohols react in 2-3 minutes and primary alcohols do not react with reagent unless the mixture is heated.

