

Unit

7

Alcohol, Phenol and Ether Compounds

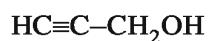
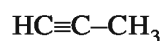
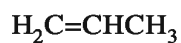
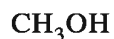
7.1 Introduction

We have learnt earlier that when one or more hydrogen atoms of a hydrocarbon, are substituted by another atom or a group of atoms (functional group) then new organic compounds are formed. When the hydrogen atom attached to saturated carbon of hydrocarbon, is substituted by hydroxyl group ($-OH$) then alcohol is formed.

e.g.,

Hydrocarbon

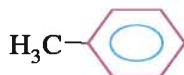
Alcohol



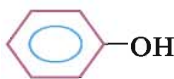
Thus, **the general formula of alcohol is $R-OH$** ; where R = alkyl group or alkenyl or alkynyl or aryalkyl group. If the hydrogen atom attached to the carbon atom of an aromatic, is substituted by hydroxyl group then phenol is formed.

e.g.,

Hydrocarbon



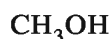
Phenol



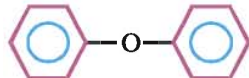
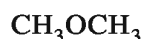
Thus, **the general formula of phenol is $\text{Ar}-\text{OH}$** ; where Ar = aryl group. If the hydrogen atom of hydroxyl group of alcohol or phenol, is substituted by alkyl or alkenyl or alkynyl or aryl group then ether is formed.

e.g.,

Alcohol/Phenol



Ether



Thus, **the general formula of ether is $\text{R}_1/\text{Ar}_1-\text{O}-\text{R}_2/\text{Ar}_2$** ; where R_1 and R_2 = alkyl or alkenyl or alkynyl group and Ar_1 and Ar_2 = aryl group.

Alcohols and ethers have same general formula $\text{C}_n\text{H}_{2n+2}\text{O}$ but due to different functional groups, they are called functional group isomers. For example, ethanol and methoxymethane have same molecular formula $\text{C}_2\text{H}_6\text{O}$ but their structural formula $\text{CH}_3\text{CH}_2\text{OH}$ and CH_3OCH_3 possess different functional groups.

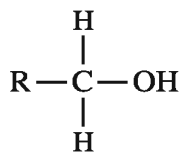
7.2 Classification of Alcohols

The classification of alcohols is carried out in three types depending on the carbon which has been attached to the hydroxyl group in structure of alcohol, viz (1) Primary (1°) alcohol, (2) Secondary (2°) alcohol and (3) Tertiary (3°) alcohol.

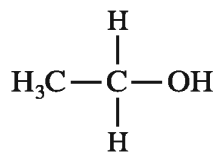
(1) Primary (1°) alcohol : Alcohol, in which the hydroxyl group is attached to primary carbon is called primary (1°) alcohol.

(2) **Secondary (2⁰) alcohol** : Alcohol, in which the hydroxyl group is attached to secondary carbon is called secondary (2⁰) alcohol.

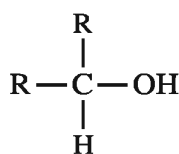
(3) **Tertiary (3⁰) alcohol** : Alcohol, in which the hydroxyl group is attached to tertiary carbon is called tertiary (3⁰) alcohol.



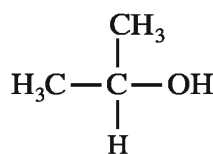
Primary (1⁰) alcohol.



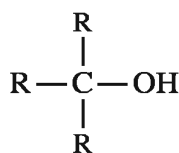
Primary (1⁰) alcohol.



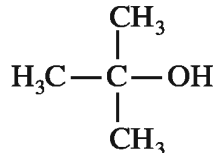
Secondary (2⁰) alcohol.



Secondary (2⁰) alcohol.



Tertiary (3⁰) alcohol.



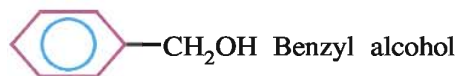
Tertiary (3⁰) alcohol.

7.3 Nomenclature of Alcohols

Common name : For the common name of alcohols, the **alcohol**, word is added after the name of hydrocarbon group which is attached to the -OH group.

e.g., CH₃OH Methyl alcohol

CH₃CH₂OH Ethyl alcohol.



IUPAC name :

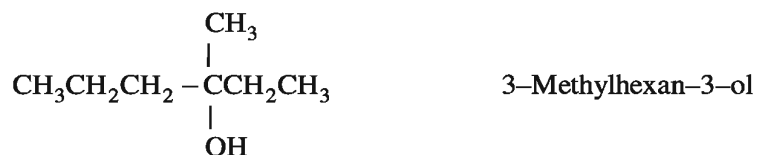
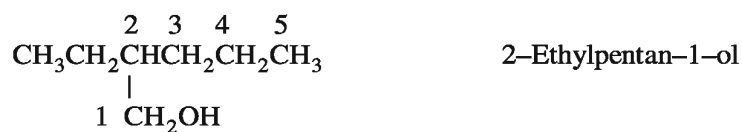
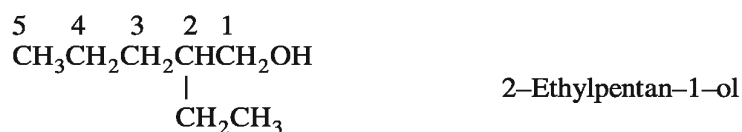
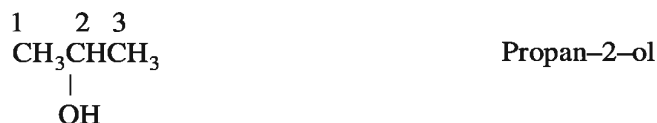
(1) In alcohol, the longest carbon chain of hydrocarbon containing hydroxyl group is selected. Then dropping the last letter 'e' from the name of hydrocarbon, the suffix 'ol' is added. For example, by dropping 'e' from methane and adding the suffix 'ol', the derived name will be **methan + ol = methanol** and in that manner from ethane, **ethan + ol = ethanol** is derived.

e.g., CH₃OH Methanol

CH₃CH₂OH Ethanol

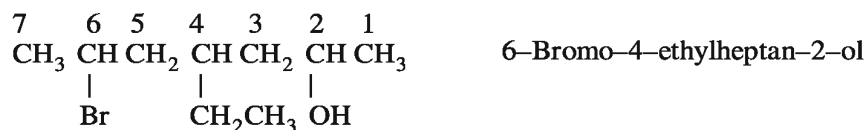
(2) In alcohols containing more than two carbon atoms the smallest number for location of the position of hydroxyl group is placed before the suffix 'ol'.

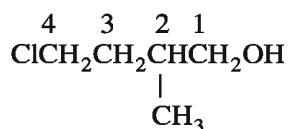
e.g.,



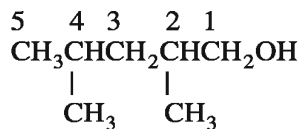
(3) If more than one substituents are present in alcohol molecule then in nomenclature they are presented in alphabetical order.

e.g.,





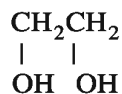
4-Chloro-2-methylbutan-1-ol



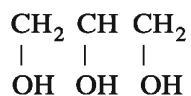
2, 4-Dimethylpentan-1-ol

(4) If alcohols containing more than one hydroxyl groups, the di, tri.....etc. prefix for two, three.... etc. number of hydroxyl groups respectively, are written before the suffix 'ol'. Here last alphabate 'e' is not removed from name of hydrocarbon.

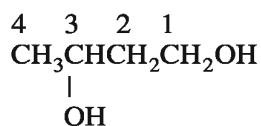
e.g.,



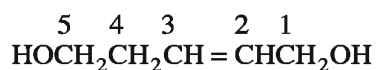
Ethane-1,2-diol



Propane-1,2,3-triol



Butane-1,3-diol



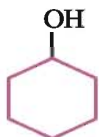
Pent-2-ene-1,5-diol

(5) In alcohols the hydroxyl group attached to the carbon of cyclic system is given the first number.

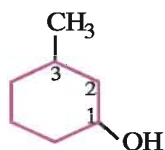
e.g.,



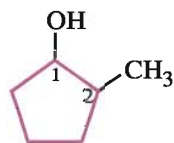
Cyclopentanol



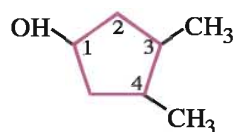
Cyclohexanol



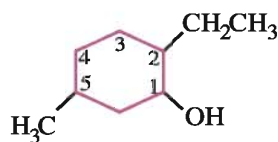
3-Methylcyclohexanol



2-Methylcyclopentanol



3,4-Dimethylcyclopentanol

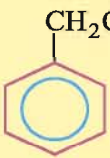


2-Ethyl-5-methylcyclohexanol

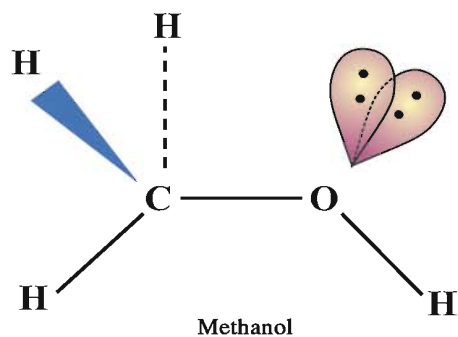
The structural formula, IUPAC name, common name, their type and boiling point of some alcohol molecules are presented in table 7.1.

Table 7.1 Alcohol compounds

Structural formula	IUPAC name	Common name	Type	Boiling point (K)
CH_3OH	Methanol	Methyl alcohol	1°	338
$\text{CH}_3\text{CH}_2\text{OH}$	Ethanol	Ethyl alcohol	1°	351
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	Propan-1-ol	n-Propyl alcohol	1°	370
$\begin{array}{c} \text{CH}_3\text{CHCH}_3 \\ \\ \text{OH} \end{array}$	Propan-2-ol	Isopropyl alcohol	2°	355
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	Butan-1-ol	n-Butyl alcohol	1°	390
$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{OH} \\ \\ \text{CH}_3 \end{array}$	2-Methylpropan-1-ol	Isobutyl alcohol	1°	381

$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHCH}_3 \\ \\ \text{OH} \end{array}$	Butan-2-ol	Secondary butyl alcohol	2 ^o	373
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\ \\ \text{OH} \end{array}$	2-Methylpropan-2-ol	Tertiary butyl alcohol	3 ^o	356
$\begin{array}{c} \text{CH}_2\text{CH}_2 \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$	Ethane-1,2-diol	Ethylene glycol	1 ^o 1 ^o	471
$\begin{array}{c} \text{CH}_2 \quad \text{CH} \quad \text{CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$	Propane-1,2,3-triol	Glycerol (Glycerine)	1 ^o 2 ^o 1 ^o	563
	Phenylmethanol	Benzyl alcohol	1 ^o	478

7.4 Electronic Structure of Alcohols

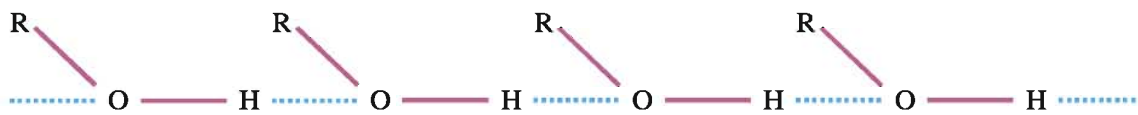


C-O and O-H	σ -bond
C and O	sp^3 hybridisation
C-O-H angle	108.5 ^o

7.5 Physical Properties of Alcohols

In alcohol compounds, the electronegativity of oxygen atom (3.5) of hydroxyl group is higher than the electronegativity of hydrogen atom (2.1). Due to this, it induces partial negative charge (δ^-) on oxygen atom and partial positive charge (δ^+) on hydrogen atom. So $\text{O}^{\delta^-}-\text{H}^{\delta^+}$ bond becomes polar and in liquid alcohols intermolecular hydrogen bond is formed, as a result intermolecular

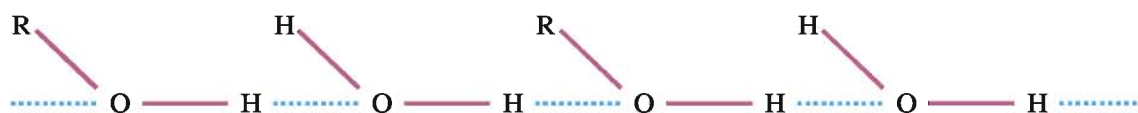
attraction increases. The higher energy is required to break these attraction forces. If there are more attractive forces in the molecules of liquid alcohol, then more thermal energy is required to break and to convert it in gaseous forms. So the values of boiling point increase. This type of hydrogen bond is not formed in alkanes because the polar bond is absent in them. Therefore **the boiling points of alcohols are higher than those of alkanes having approximately equal molecular mass.** e.g., boiling point of ethanol (molecular mass = 46 gram mole⁻¹, b.p. = 351 K) is higher than that of propane (molecular mass = 44 gram mole⁻¹, b.p. = 231 K) and boiling point of propanol (molecular mass = 60 gram mole⁻¹, b.p. = 370 K) is higher than that of butane (molecular mass = 58 gram mole⁻¹, b.p. = 273 K).



Intermolecular hydrogen bond between alcohol molecules

In linear series of primary alcohols, the boiling point increases gradually as the number of carbon atoms increases; because increasing with the number of carbon, intermolecular distance is decreased, as a result intermolecular attraction forces increase. e.g., while going from methanol to butan-1-ol, the boiling point gradually increases (Table 7.1), as compared to primary (1^o) alcohols containing three or more than three carbon atoms and with the same molecular formula, in secondary (2^o) alcohol and as compared to secondary (2^o) alcohol, in tertiary (3^o) alcohols having more branched chains. As a result it decreases the area of surface and decreases the intermolecular attraction with increase in intermolecular distance. Therefore **among alcohols containing same molecular formula, secondary alcohol has lower boiling point than primary alcohol and tertiary alcohol has lower boiling point than secondary alcohol.** This is due to decrease in the intermolecular attraction. e.g., boiling point of propan-2-ol (secondary) (b.p. 355 K) is lower than that of propan-1-ol (primary) (b.p. 370 K) and alcohols having molecular formula C₄H₉OH have three isomers butan-1-ol (primary) (b.p. 390 K), butan-2-ol (secondary) (b.p. 373 K) and 2-methyl propan-2-ol (tertiary) (b.p. 356 K) whose boiling points are decreasing respectively.

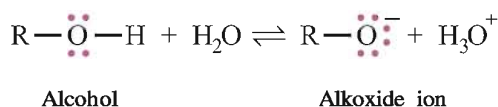
In aqueous solution of alcohols, the intermolecular attraction between them increases due to the formation of hydrogen bond between polar molecule water and polar molecule alcohol. Therefore, lower molecular mass containing methanol and ethanol are more soluble in water. As the number of carbon atoms of hydrocarbon group in alcohol increases, the molecular masses also increase; as a result solubility in water decreases, because of formation of hydrogen bond cannot be possible with an increase in length of chain.



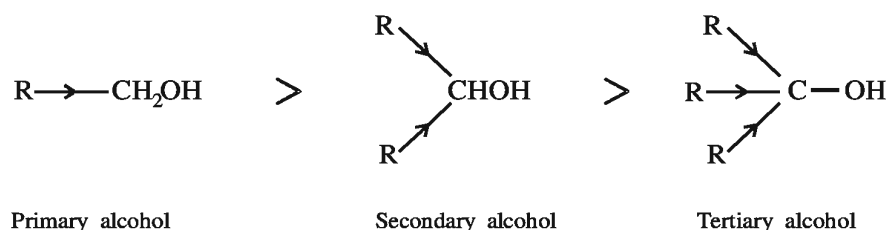
Intermolecular hydrogen bond between alcohol and water molecules

As we studied earlier, there is formation of hydrogen bond between two molecules of alcohol and the alcohol and water molecules. This results in the **increase in the boiling point and solubility in water with increase in number of hydroxyl groups in alcohols.** For example, boiling points and solubilities in water of ethanol (b.p. 351 K), ethane-1,2-diol (b.p. 471 K) and propane-1,2,3-triol (b.p. 563 K) increase gradually.

Acidity of Alcohols : Aqueous solution of alcohols possess slight acidic property due to polar O–H bond present in them. Alcohols have acidic property similar to that of water. Most of alcohols (except methanol) are less acidic than water.



In alcohol compounds, an electron releasing group–R(–CH₃, –C₂H₅) increases the electron density of O–H bond, so results in decrease of the polarity of O–H bond. As a result the acidic property decreases. Thus, the order of acidic strength of alcohol compounds is,

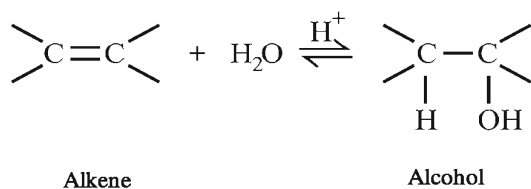


7.6 Preparation of Alcohols

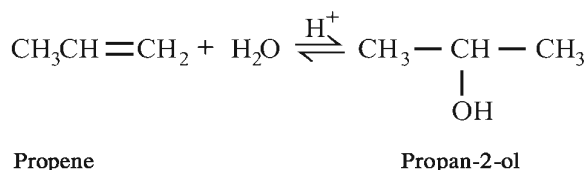
Alcohols can be prepared by different methods,

(1) Alcohol from alkene compounds :

(i) By acid catalysed hydration : Alkene compounds form alcohols by reaction with water in presence of acid catalyst.

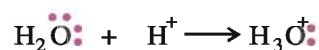


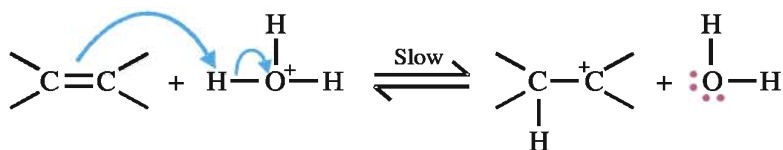
If unsymmetrical alkene is used as a starting material then the addition reaction follows the **Markonikov's rule** and give alcohols.



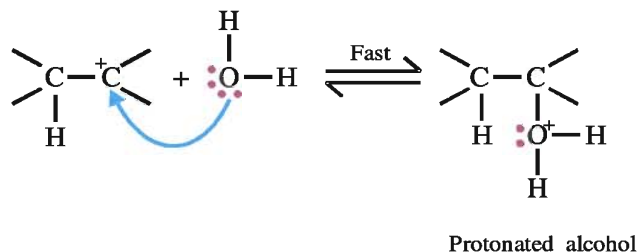
Mechanism :

Step-1 : Alkene molecule accepts a proton from aqueous acid H₃O⁺ and forms carbocation.

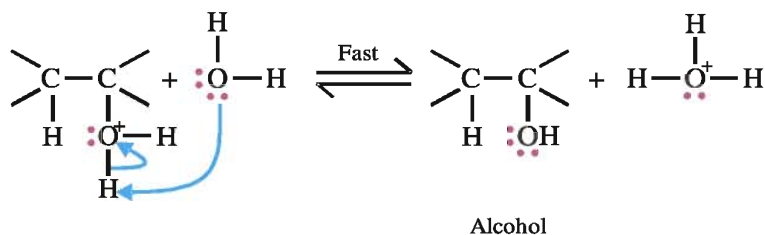




Step-2 : Nucleophilic reagent (water) attacks on carbocation and forms protonated alcohol.

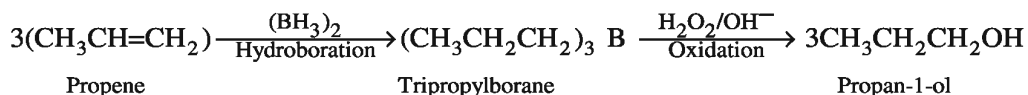


Step-3 : Proton is removed and an alcohol is formed



Note : Concept about drawing of Curved Arrow (\curvearrowright): It is easy to understand the transfer of electrons by curved arrow (\curvearrowright or \curvearrowleft) in the mechanism of reaction. This curved arrow is always drawn away from more electron containing (generally negatively charged) species towards a less electron containing (generally positively charged) species. The arrow starts from the electron source (electron pair or bond). It does not start from an atom. This curved arrow does not indicate the transfer of an atom.

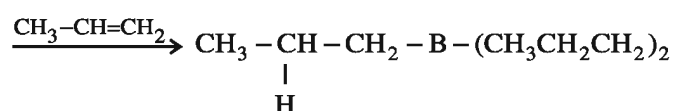
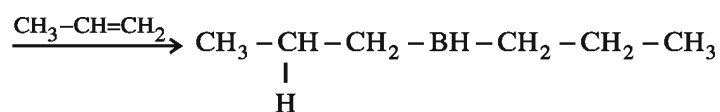
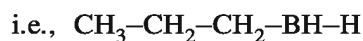
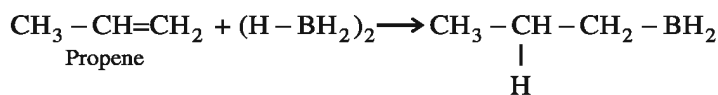
(ii) By hydroboration-oxidation : For the preparation of alcohol in laboratory, the indirect addition of water in alkene compounds can be achieved in presence of diborane (BH_3)₂. Diborane reacts with alkenes to give trialkylborane as addition product, which is called hydroboration reaction. Trialkylborane is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.



Mechanism :

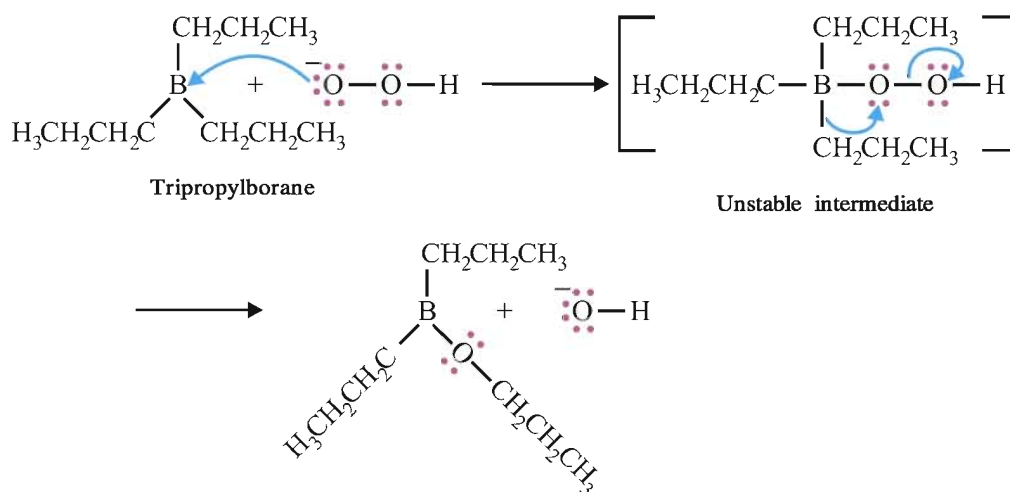
Step-1 : Alk-1-ene like propene reacts with diborane and forms trialkylborane. It is the result of addition of boron hydride to double bond of three molecules of alk-1-ene. This hydroboration reaction follows the **anti-Markonikov rule**. So, boron atom gets attached to the carbon atom

involved in double bond in alkene with more hydrogen atoms and hydrogen gets attached to the carbon atom with fewer hydrogen atoms.

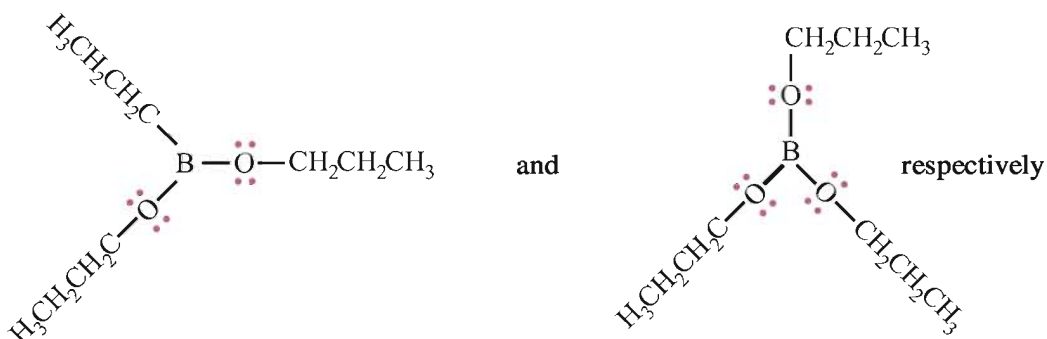


(Tripropylborane)

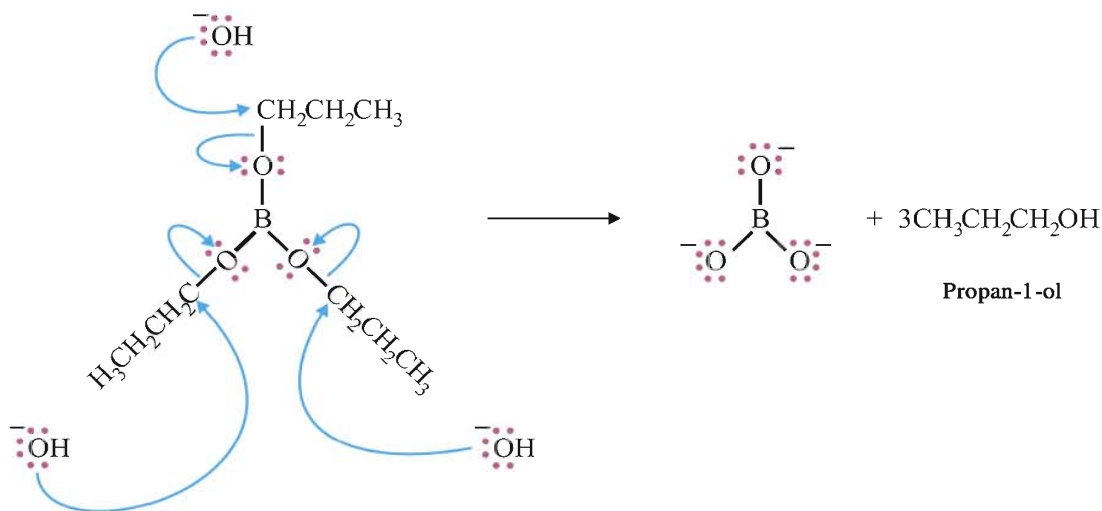
Step-2 : Tripropyl borane is oxidised to tripropyl borate by of hydrogen peroxide.



Two times repetition of this reaction forms

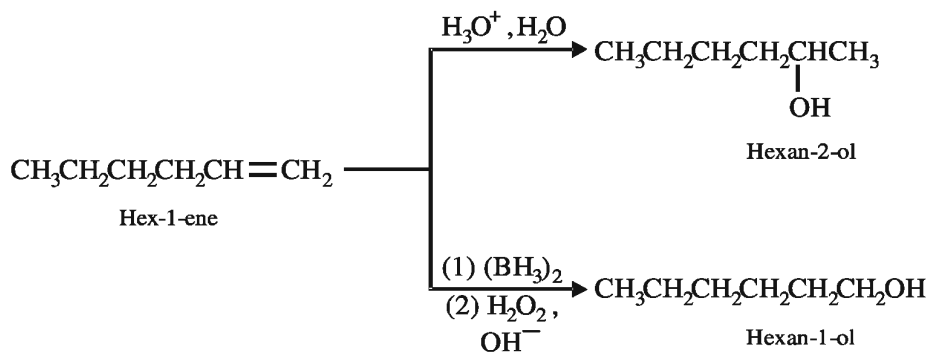


Step-3 : The hydrolysis of tripropylborate forms three molecules of propan-1-ol and borate ion in basic medium.



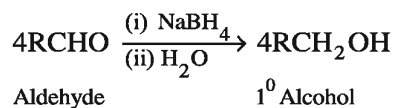
Thus, during the preparation of alcohols by acid catalysed hydration, the -OH group gets attached to the carbon atom involved in double bond of alkene, with fewer hydrogen atoms. In contrast to this, during the preparation of alcohols by hydroboration-oxidation, the -OH group gets attached to the carbon atom involved in double bond of alkene with more hydrogen atoms.

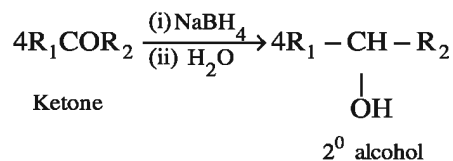
e.g.,



(2) Alcohols from carbonyl compounds :

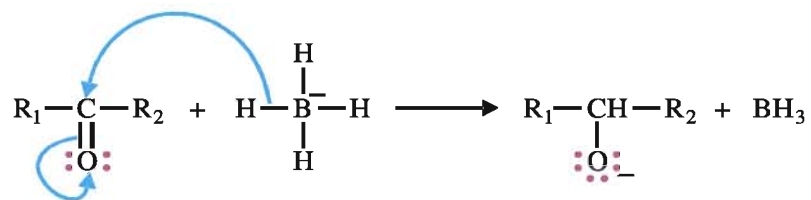
(i) **By reduction of aldehydes and ketones :** Alcohols can be obtained by reduction of aldehydes and ketones with sodium borohydride (NaBH_4) or lithium aluminium hydride (LiAlH_4).
Reduction of aldehyde gives 1^o alcohol and reduction of ketone gives 2^o alcohol.



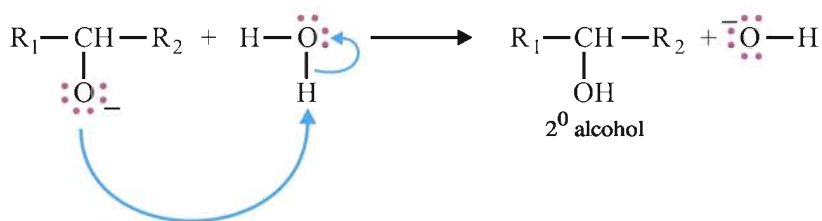


Mechanism :

Step-1 : Hydride ion ($:H^-$) of sodium borohydride reagent combines with carbonyl carbon and forms alkoxide ion.

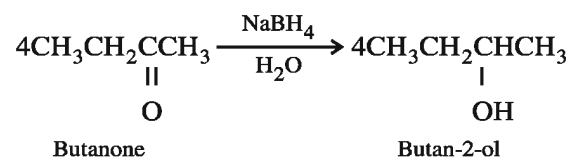
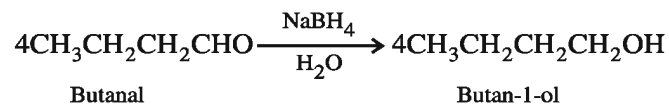


Step-2 : Alkoxide ion reacts with water and forms alcohol.

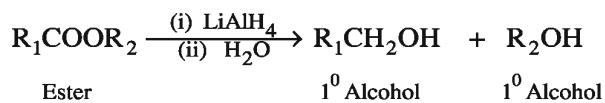
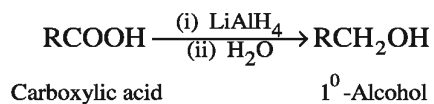


If the reaction is repeated three times more then as a result four moles of ketone form four moles of 2^0 alcohols. For this 1 mole of sodium borohydride is consumed.

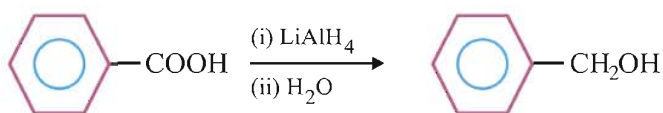
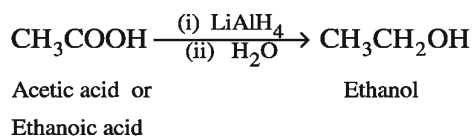
In this mechanism, putting the H instead of R_2 the mechanism of formation of alcohols by reduction of aldehyde can be understood.



(ii) By reduction of carboxylic acids or esters : Reduction of carboxylic acids and esters is achieved by use of strong reducing agent like lithium aluminium hydride and primary alcohols can be obtained.

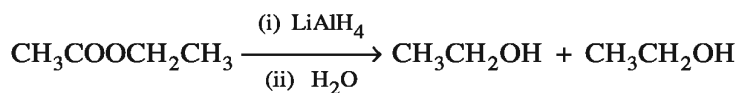


e.g.,



Benzoic acid

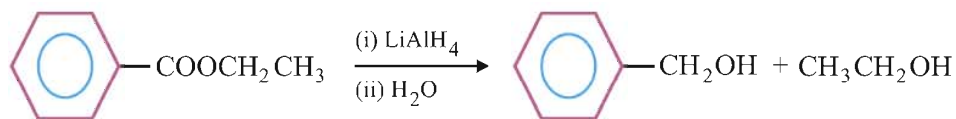
Phenylmethanol
(Benzyl alcohol)



Ethylethanoate
(Ethyl acetate)

Ethanol

Ethanol



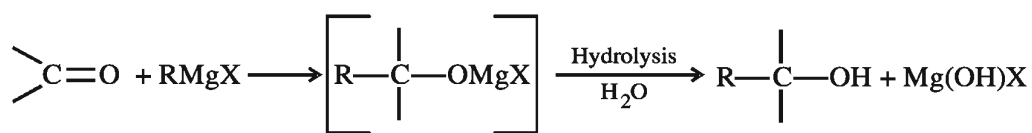
Ethylbenzoate

Phenylmethanol

Ethanol

(3) Alcohols by Grignard reagents :

If Grignard reagents are added to carbonyl compounds then 1^o, 2^o and 3^o alcohols are formed.



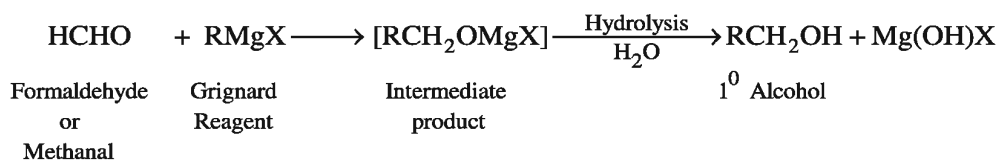
Carbonyl
compounds

Grignard
Reagent

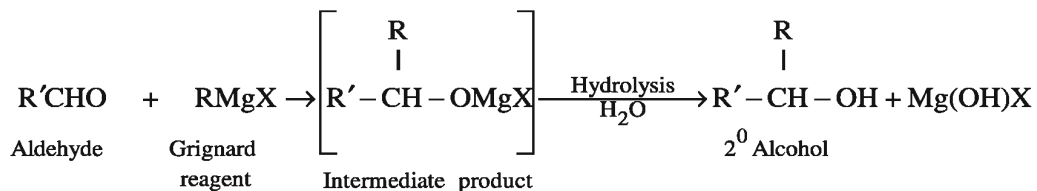
Intermediate product

Alcohol

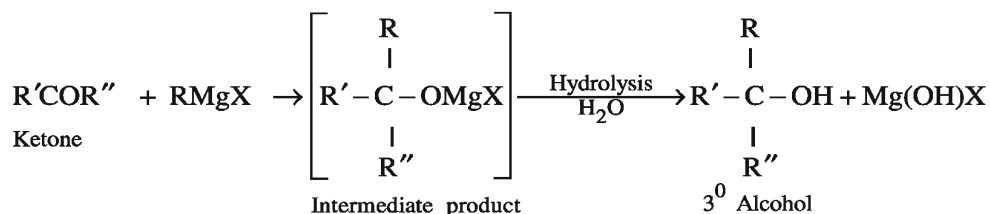
(i) Grignard reagent reacts with formaldehyde and gives 1^o alcohol.



(ii) Grignard reagent reacts with aldehyde compounds except formaldehyde and forms 2^o alcohols.

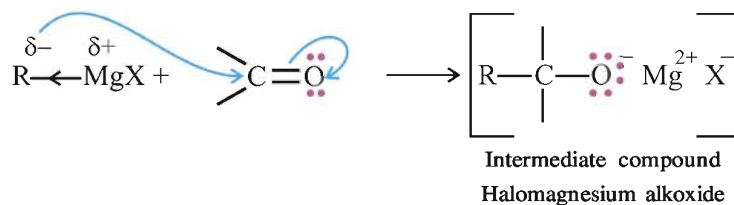


(iii) Grignard reagent reacts with ketone compounds and forms 3^o alcohols.

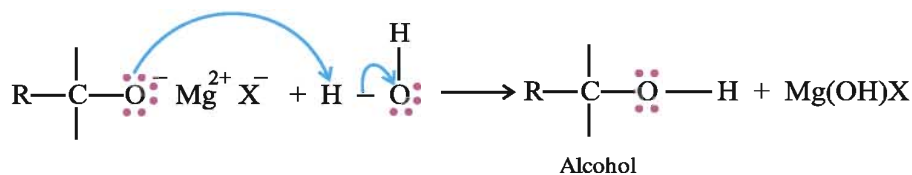


Mechanism :

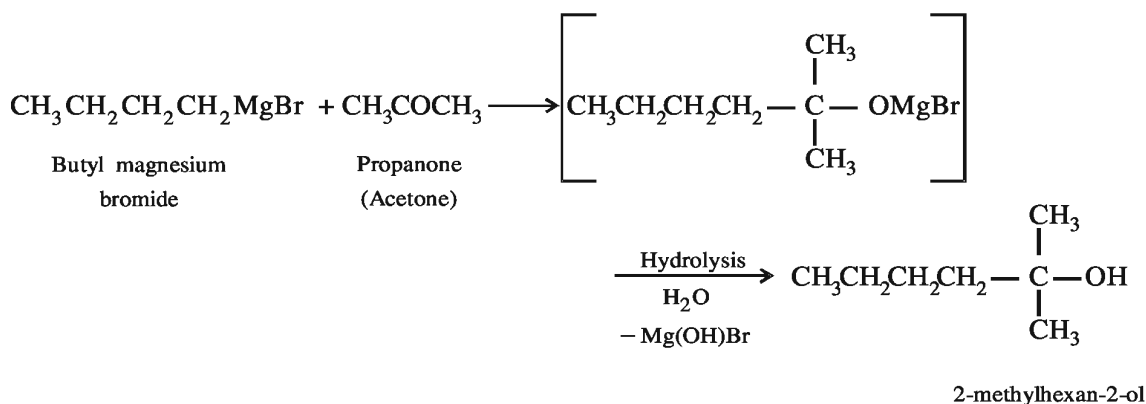
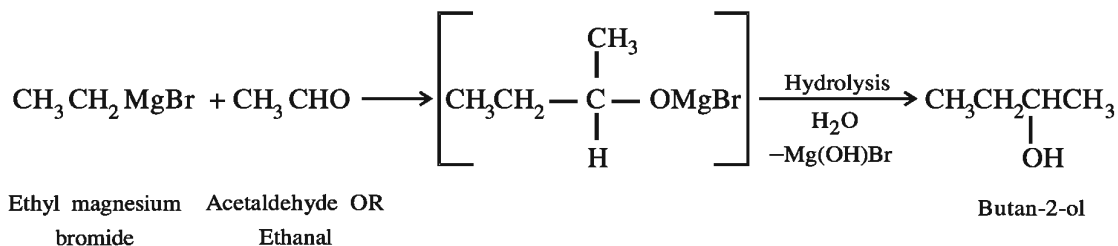
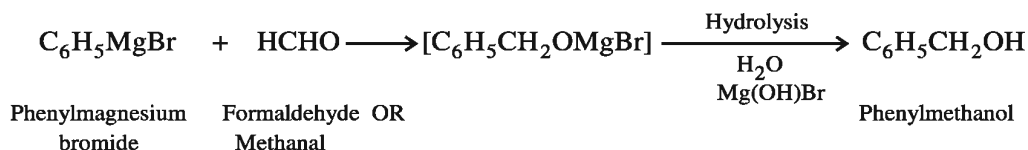
Step-1 : Grignard reagent is added to carbonyl compound and it forms intermediate compound. In Grignard reagent RMgX, the electronegativity (2.5) of carbon atom in R is higher than electronegativity (1.2) of magnesium atom and as a result the common electron pair of bond R–Mg is more attracted towards R, due to this partial negative charge on R and partial positive charge on Mg atom are induced.



Step-2 : Intermediate product reacts with water and forms alcohol.

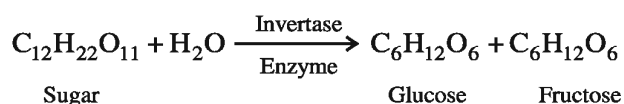


Examples of alcohols formed by Grignard reagent

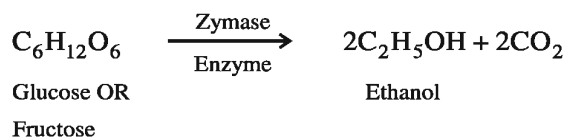


(4) Preparation of alcohol by fermentation method :

Fermentation method is most useful for preparation of ethanol. This method is extensively used for industrial production of ethanol. Sugar present in molasses is fermented by enzyme invertase, as a result glucose and fructose are formed.



Glucose and fructose are fermented by enzyme zymase found in yeast; due to this ethanol and carbon dioxide gas are formed.



Distillation of final solution produces an azeotropic mixture of 95% ethanol and 5% water i.e. only one component $\text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$ is produced. Pure ethanol is obtained by membrane technology.

Pure ethanol is a colourless liquid. Its boiling point is 351 K. It is used as a solvent in paint industry. It is also used in preparation of a number of organic compounds.

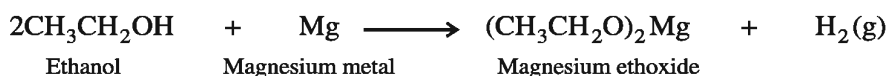
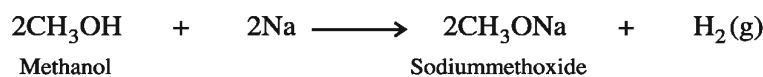
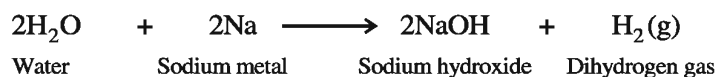
7.7 Chemical Reactions of Alcohols

There are two types of reactions in alcohols. Looking to the structure R–O–H in some reactions O–H bond is broken and in others R–O bond is broken. These reactions form different types of compounds.

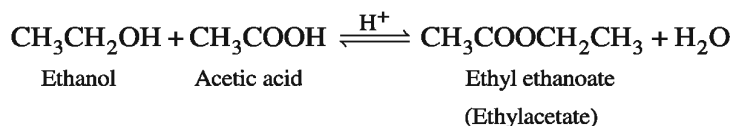
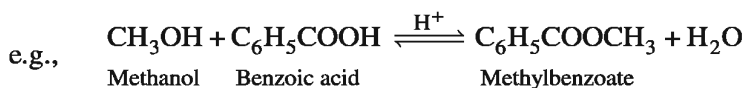
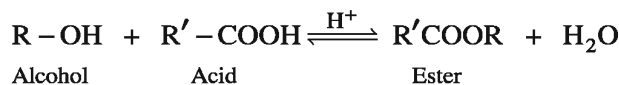
(1) Reactions involving cleavage of O–H bond :

(i) **Reaction of alcohol with active metals** : Like water, alcohols react with Li, Na, K, Mg, Al and other active metals to liberate dihydrogen gas and form metal alkoxides. These metal alkoxides act as stronger base than sodium hydroxide.

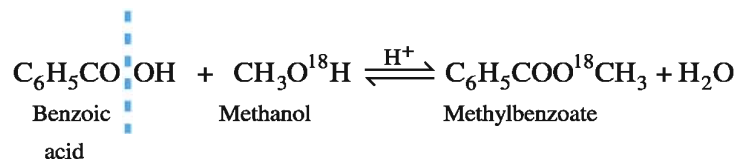
e.g.,



(ii) **Reaction of alcohol with acids** : Alcohols react with carboxylic acids in presence of acid catalyst to form esters through a condensation reaction. It is called **esterification**.

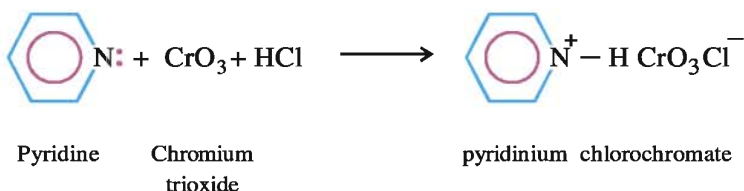
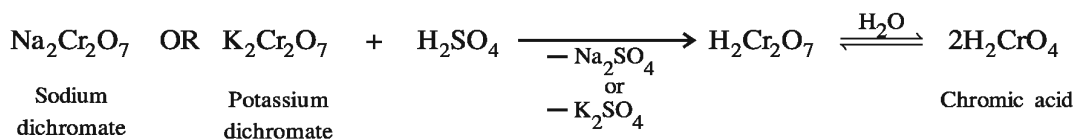


When benzoic acid reacts with methanol that has been labelled with radioactive O^{18} , the labelled O^{18} appears in the ester product. It is indicated that during the esterification the aggregate water molecule is removed as OH^- is removed from acid molecule and H^+ is removed from alcohol molecule.

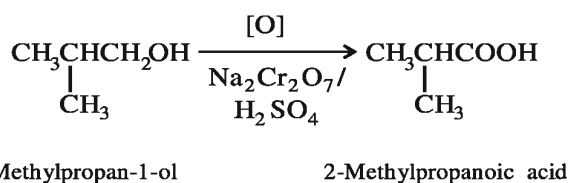
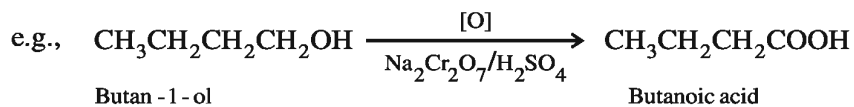
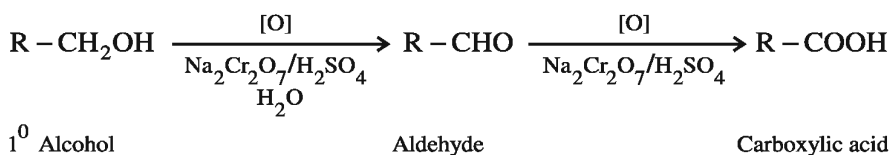


(iii) **Oxidation of alcohols** : During the oxidation of alcohols, one or more hydrogen atoms are lost from the carbon bearing the –OH group. The products obtained by oxidation of alcohols depend upon

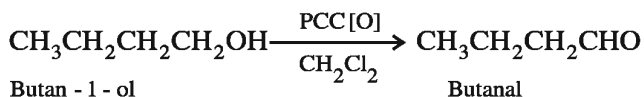
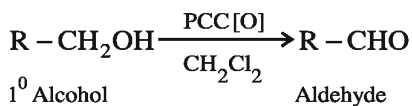
the type of alcohols and reagents. The reagents most commonly used as oxidising agents for the oxidation of alcohols are **chromic acid (H_2CrO_4)** or **potassium permanganate (KMnO_4)** or **pyridinium chlorochromate (PCC)**.

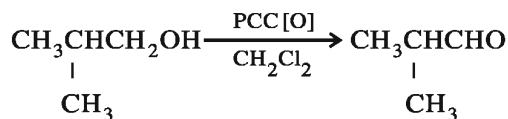


The primary alcohol is oxidised by KMnO_4 or H_2CrO_4 initially to an aldehyde. However, this aldehyde is very difficult to obtain as product because this aldehyde is more easily oxidised than the alcohol and so is converted rapidly to the carboxylic acid. Thus, **the normal product of oxidation of 1° alcohol with a strong oxidizing agent like KMnO_4 or H_2CrO_4 is a carboxylic acid.**



1° alcohol is oxidised by mild oxidizing agent like pyridinium chloro-chromate (PCC) and aldehyde is formed. Then after oxidation of aldehyde does not occur. This reaction is carried out in an anhydrous solvent such as dichloromethane (CH_2Cl_2).

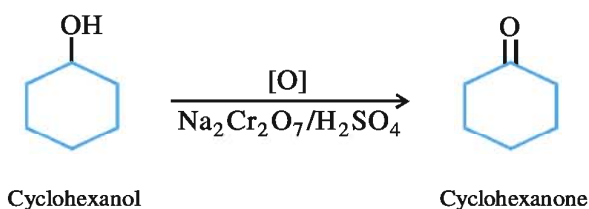
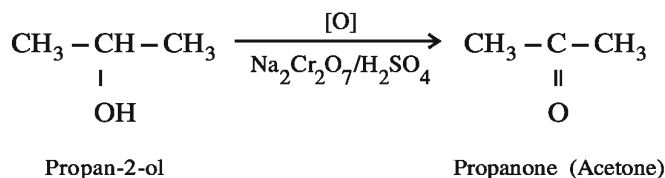
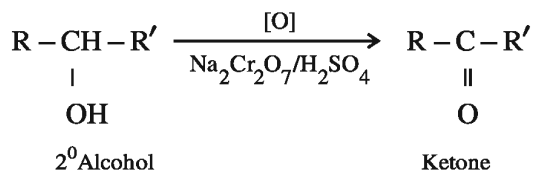




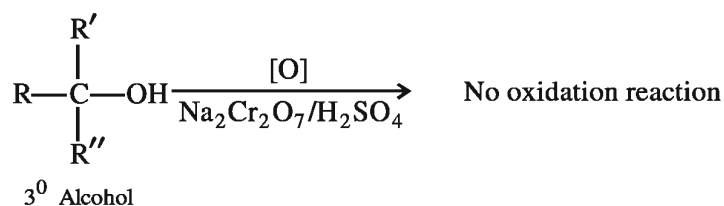
2-Methylpropan-1-ol

2-Methylpropanal

2° Alcohols are oxidised by H_2CrO_4 or KMnO_4 and form ketones.

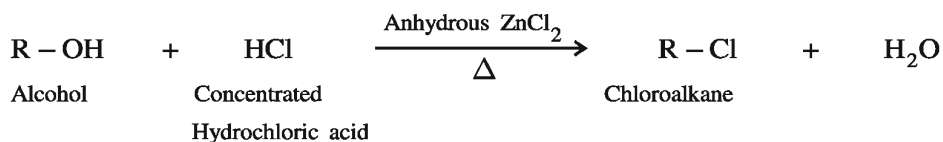


In 3° alcohols, the carbon bearing the $-\text{OH}$ group has no hydrogen, so they are not oxidized by strong oxidizing agents.



(2) Reactions involving cleavage of C–O bond :

(i) Reaction of alcohol with halogen acid : Alcohol when heated with concentrated hydrochloric acid in presence of anhydrous zinc chloride gives chloro alkane. This reaction is fast with tertiary alcohols, slow with secondary alcohols and difficult with primary alcohols.

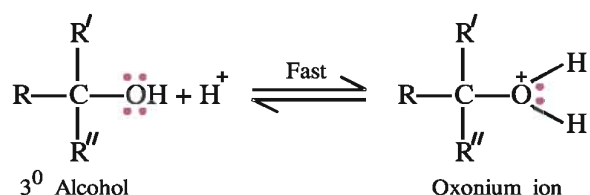


In laboratory primary, secondary and tertiary alcohols can be detected by this reaction and the method to do so is called **Lucas test**. In this test, a given sample of alcohol is mixed, shaken and

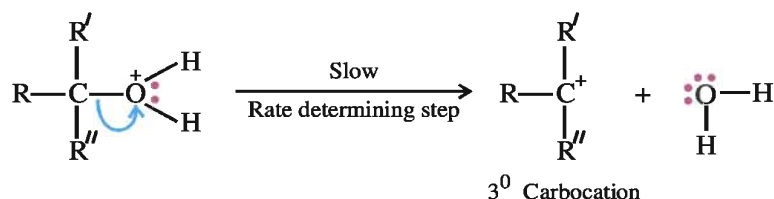
warmed slightly with anhydrous zinc chloride and concentrated hydrochloric acid and kept for some time. If an oily drop appears in short time on the upper layer of the mixture, it must be 3^o alcohol, if it takes about five minutes to become milky, it must be 2^o alcohol; if mixture remains clear without any reaction, it must be 1^o alcohol. We will understand mechanism of reaction of tertiary alcohol with concentrated hydrochloric acid.

Mechanism :

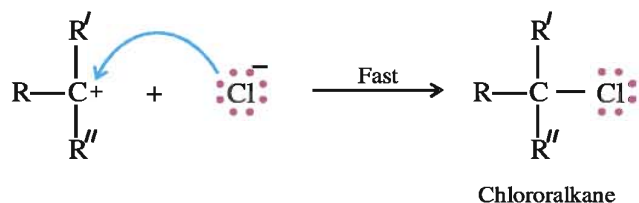
Step-1 : Tertiary alcohol is converted into an oxonium ion through protonation by H⁺ of acid. This step is fast.



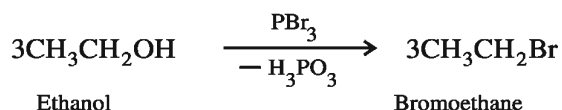
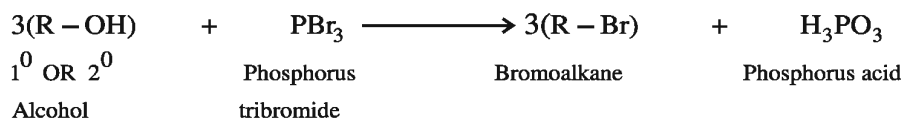
Step-2 : 3^o carbocation is formed by the loss of a water molecule from the oxonium ion. This step is slow so it is called the rate determining step.

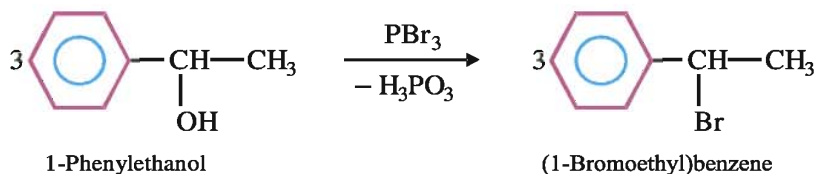
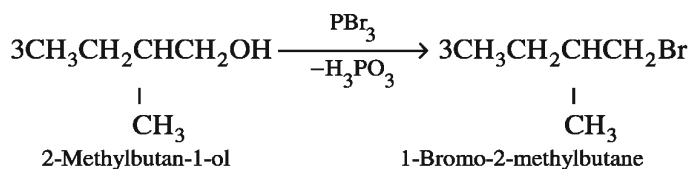


Step-3 : 3^o carbocation reacts with Cl⁻ rapidly and forms chloroalkane.



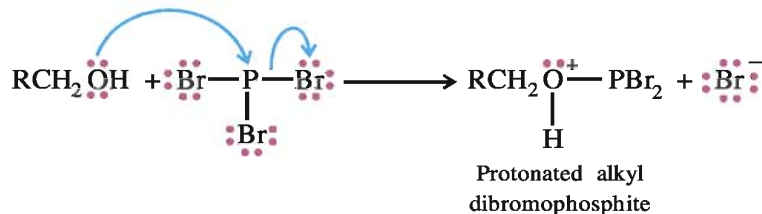
(ii) Reaction of alcohol with phosphorus tribromide : 1^o and 2^o alcohols react with phosphorus tribromide to form bromoalkane.



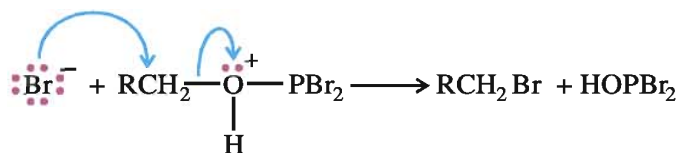


Mechanism :

Step-1 : Alcohol reacts with phosphorus tribromide and as a result intermediate compound alkyl dibromophosphate is formed.

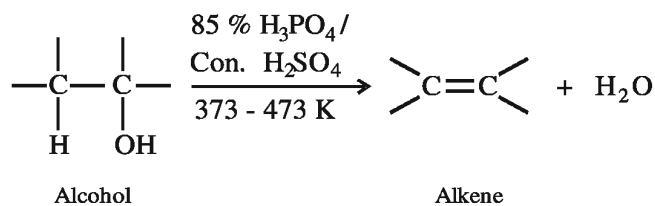


Step-2 : Bromide ion attacks on carbon atom and forms haloalkane.

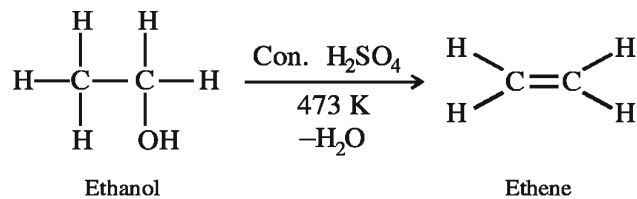


This HOPBr₂ reacts with other molecules of alcohol. Thus, at the end of the reaction three moles of haloalkanes are formed from three moles of alcohols. For this 1 mole of phosphorus tribromide is consumed.

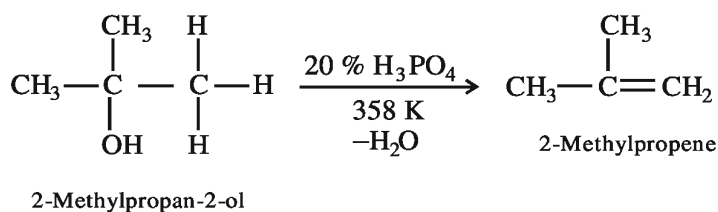
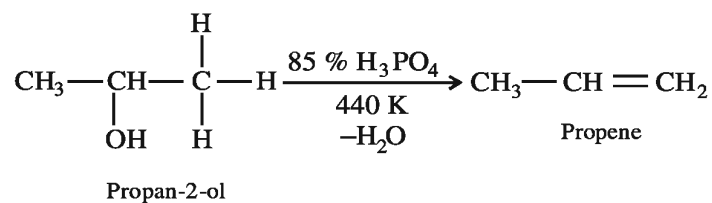
(iii) Dehydration of alcohols : An alkene is formed by elimination of a molecule of water from adjacent carbon atoms of an alcohol. **Elimination of a molecule of water is called dehydration.** In the laboratory, dehydration of alcohol is carried out by heating it in presence of 85 % phosphoric acid or concentrated sulphuric acid at 373 K to 473 K.



Ethanol (primary alcohol) is converted into ethene by heating it at 473 K.



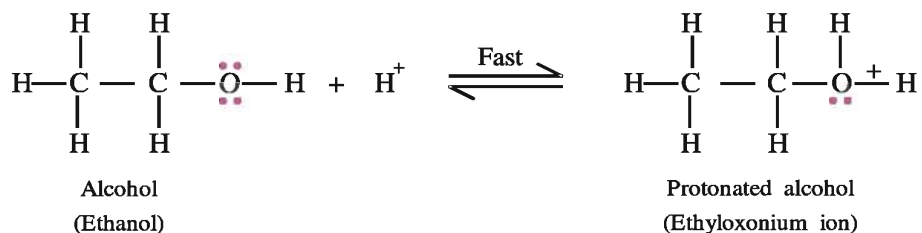
2^o and 3^o alcohols give dehydration reaction under milder conditions.



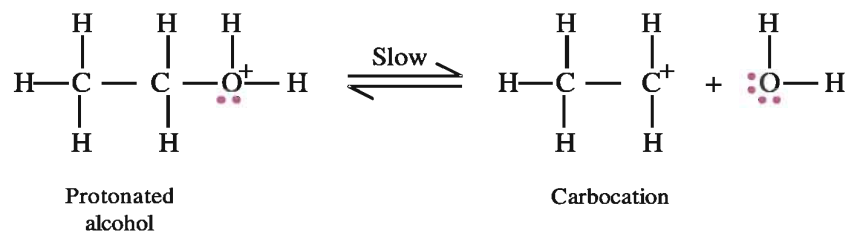
Thus, the order of ease of dehydration reaction of alcohols is 3^o alcohol > 2^o alcohol > 1^o alcohol. Here we will understand mechanism of dehydration reaction of ethanol.

Mechanism :

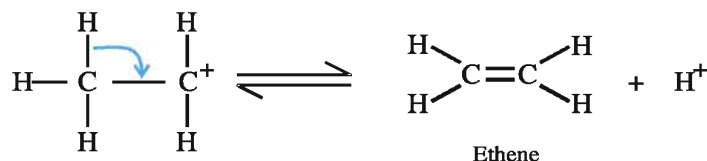
Step-1 : Ethanol is converted into ethyl oxonium ion through protonation by H⁺ of acid.



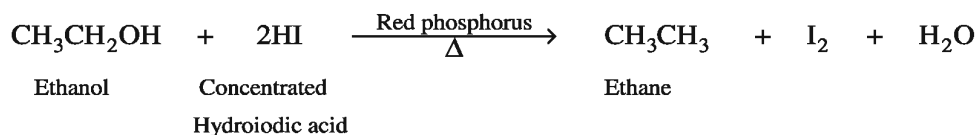
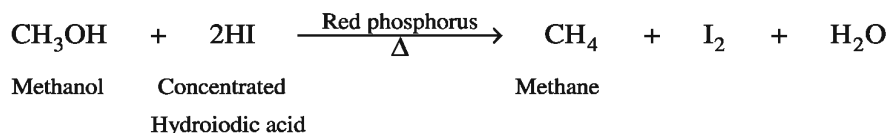
Step-2 : Carbocation is formed by the loss of a water molecule from the ethyloxonium ion. This step is slow so it is called rate determining step.



Step-3 : Ethene is formed by elimination of a proton from carbocation.



(iv) **Reduction of alcohols** : Reduction of alcohols by heating with red phosphorus and concentrated hydroiodic acid in a closed vessel give alkanes. By this reduction reaction, methanol gives methane and ethanol gives ethane.

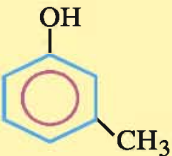

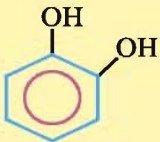
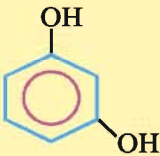

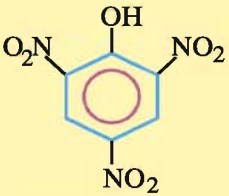
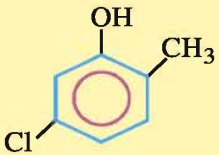


7.8 Nomenclature of Phenols

Phenol and some of its derivatives are known by their common names. e.g., Phenol, ortho-cresol, meta-cresol, para-cresol, catechol, resorcinol, hydroquinone, picric acid etc. The common names of phenol are also accepted as IUPAC names. For IUPAC nomenclature of phenol derivatives, to consider the phenol as parent hydrocarbon and mention the position of substituted other groups in aromatic ring. For this –OH group is attached to which carbon, the first number is given to it. Ortho (1, 2-disubstituted), meta (1,3-disubstituted), para (1,4-disubstituted) words are used to mention the position of substituted groups in common name. Substituted groups are written in alphabetical order. The structural formula, IUPAC name, common name of some phenol compounds are presented in table 7.2.

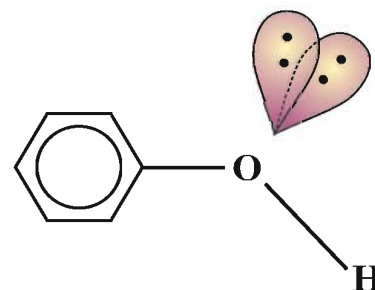
Table 7.2 Phenol compounds

Structural formula	IUPAC name	Common name
	Phenol	Phenol
	2-Methylphenol	o-Cresol

	3-Methylphenol	m-Cresol
	4-Methylphenol	p-Cresol
	Benzene -1, 2-diol	Catechol
	Benzene -1, 3-diol	Resorcinol
	Benzene -1, 4-diol	Hydroquinone (Quinol)
	2,4,6,- Trinitrophenol	Picric acid
	5-Chloro -2-methylphenol	-

7.9 Electronic Structure of Phenol

C–O and O–H	σ -bond
C sp^2 hybridisation	O sp^3 hybridisation
C–O–H angle	109°

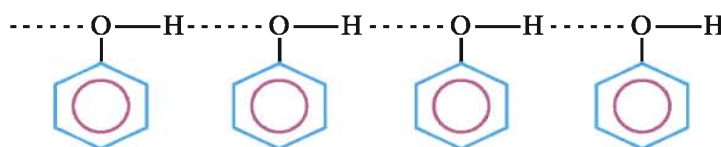


7.10 Physical Properties of Phenols

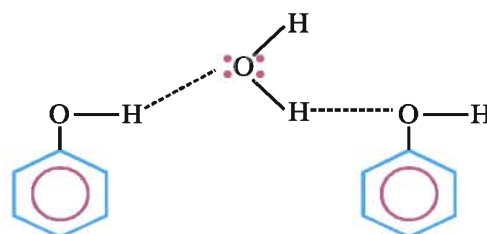
Phenol contains hydroxyl group, therefore in liquid state it forms intermolecular hydrogen bond with other molecule of phenol and with water molecule just like alcohols. Hence intermolecular attraction is increased. Due to this, phenol has higher boiling point and more solubility in water than toluene (arene compounds) and fluorobenzene (haloarene compounds) having approximately same molecular mass (table 7.3).

Table 7.3 Comparison of physical properties of phenol, arene and haloarene compounds (298 K)

Physical property	Compounds		
	Phenol	Toluene	Fluorobenzene
Molecular mass (gram mole^{-1})	94	92	96
Boiling point (K)	455	384	358
Solubility in water (Gram/100 ml)	8.2	0.05	0.2



Intermolecular hydrogen bond among the phenol molecules

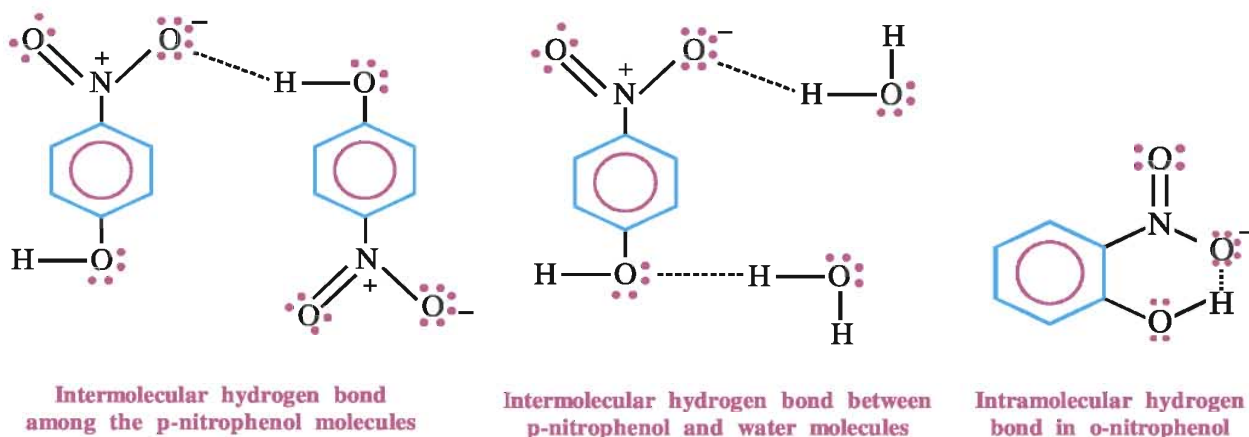


Intermolecular hydrogen bond between phenol and water molecules

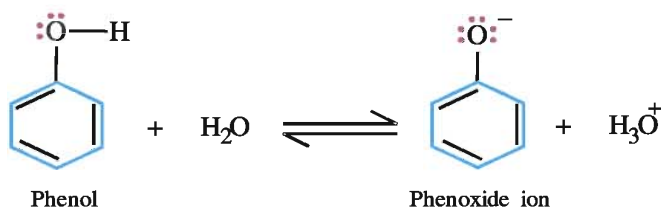
Some ortho substituted phenols like o-nitrophenol has lower melting point and less solubility in water than its m- and p- isomers (table 7.4), because m- and p- nitrophenol form intermolecular hydrogen bond with their other molecules and water molecule. But in o-nitrophenol the intramolecular hydrogen bond is formed. The hydrogen atom of hydroxyl group engaged in this bond cannot form intermolecular hydrogen bond with other molecule of o-nitrophenol and water molecule.

Table 7.4 Physical properties of isomers of nitrophenols (298 K)

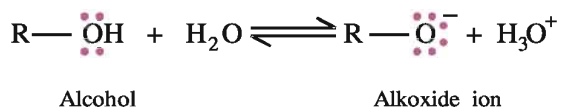
Compound	Physical properties	
	Melting point (K)	Solubility in water (gram/100 ml)
o-Nitrophenol	45	0.2
m-Nitrophenol	96	1.4
p-Nitrophenol	114	1.7



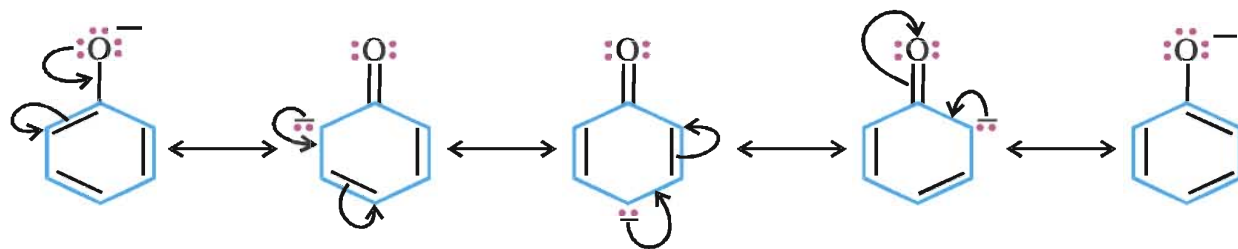
Acidity of phenol : Aqueous solution of phenol changes blue litmus paper into red. Moreover it is neutralised with solution of sodium hydroxide, but not with a solution of sodium carbonate. It indicates that phenol possesses weak acidic nature. Polar O–H bond present in phenol is responsible for acidity.



Here naturally a question will arise that which of the two from alcohol and phenol will have more acidity ? We will think about this. As we discussed previously the alkoxide ion is formed from alcohol.



In alkoxide the negative charge is localised on oxygen atom, that is its resonance forms are not possible. In phenoxide ion the negative charge on an oxygen atom becomes delocalised. Due to this more than one resonance forms of phenoxide ion are possible. Therefore stability of phenoxide ion is higher than that of alkoxide ion.

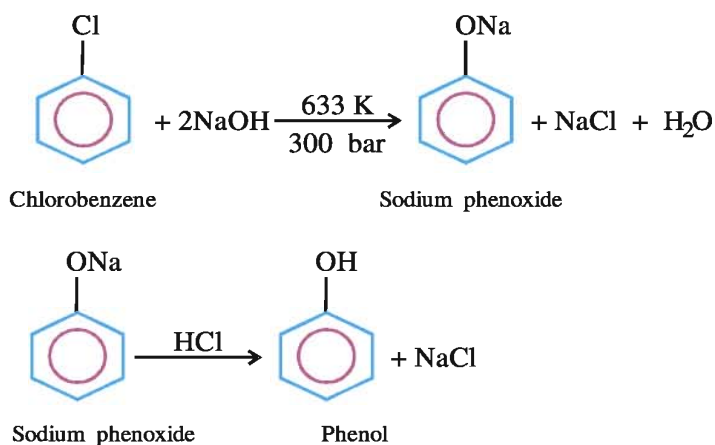


Due to higher stability of phenoxide ion, its reaction with H_3O^+ to form phenol means reverse reaction is less easy as compared to alkoxide ion. So, concentration of H_3O^+ is higher in aqueous solution of phenol than in aqueous solution of alcohol. Therefore **aqueous solution of phenol is more acidic than alcohol.**

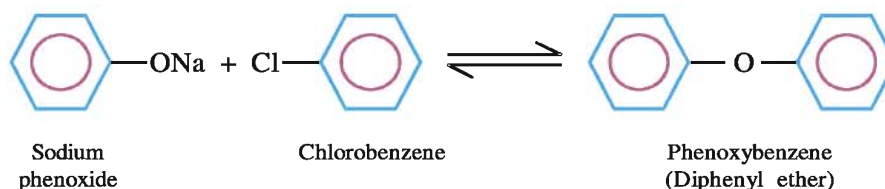
7.11 Preparation of Phenol

Phenol is most important chemical for industries. It is being used in manufacture of some dyes, drugs and polymer compounds. Phenol can be produced by different processes.

(1) Dow process : This process is used for industrial production of phenol. In this process a mixture of chlorobenzene and 6-8 % aqueous solution of sodium hydroxide is heated in a closed vessel at 300 bar pressure and 633 K as a result the sodium salt of phenol (sodium phenoxide) is produced as an intermediate product. Excess of chlorobenzene is removed from reaction mixture and acid is added into remaining solution to obtain phenol.

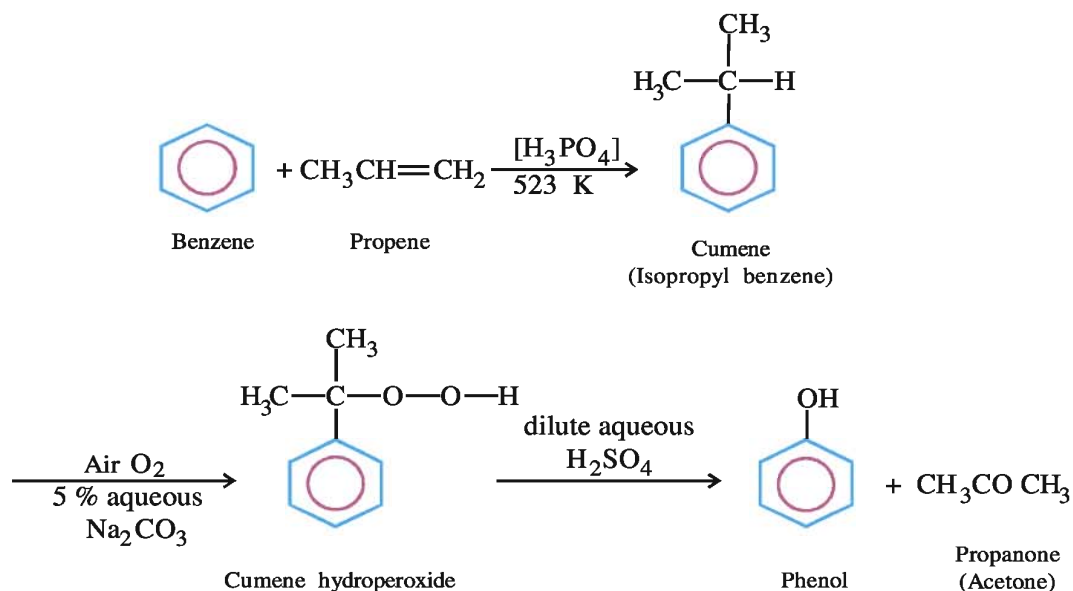


During this reaction sodium phenoxide and remaining chlorobenzene react with each other and produce phenoxybenzene (diphenyl ether) as a by-product. It decreases production of phenol. To overcome this difficulty, phenoxybenzene (diphenylether) is added into reaction mixture before carrying out reaction. Therefore according to principle of Le Chatelier the proportion of by-product is decreased, because following reaction occurs in reverse direction.

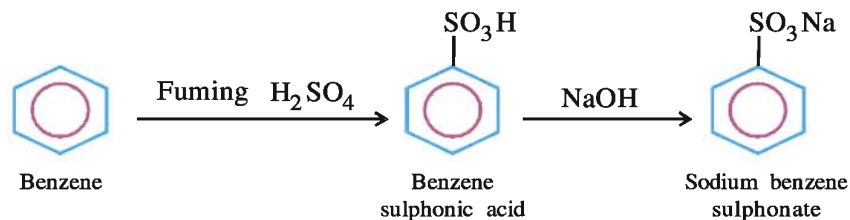


(2) Cumene Process : In this process a mixture of benzene and propene is heated at 523 K in a closed vessel in presence of phosphoric acid (H_3PO_4) catalyst to form cumene (isopropylbenzene). On passing air in a mixture of cumene and 5% aqueous sodium carbonate solution, cumene hydroperoxide is formed by oxidation. It is reacted with dilute sulphuric acid to form phenol and propanone (acetone). In this process propanone is obtained as a by-product. It is a useful solvent.

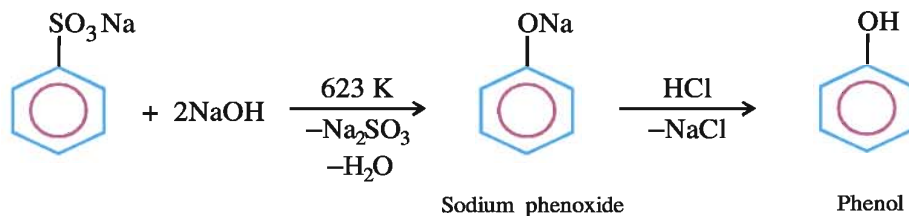
By this process highly pure phenol can be produced with less cost. Therefore most commonly this method is used for industrial production of phenol.



(3) Phenol from sodium benzene sulphonate : Benzene is reacted with fuming H_2SO_4 and then with NaOH gradually to form sodium benzene sulphonate.

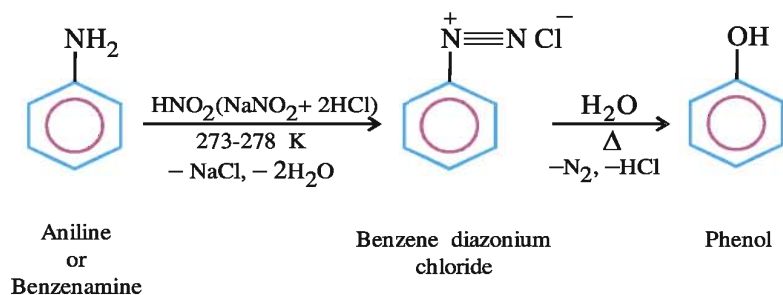


Sodium benzene sulphonate is melted with sodium hydroxide at 623 K temperature to obtain sodium phenoxide. It is reacted with acid and phenol is formed.



In 1890 this method was developed first of all in Germany for production of phenol.

(4) Phenol from diazonium salt : Aniline reacts with nitrous acid– HNO_2 ($\text{NaNO}_2 + \text{HCl}$) at lower temperature to form benzene diazonium chloride and heated it with water to form phenol.



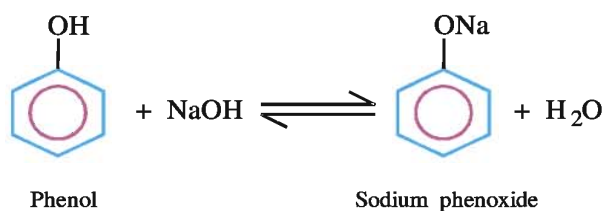
7.12 Chemical Reactions of Phenol

Two types of reactions are possible in phenol :

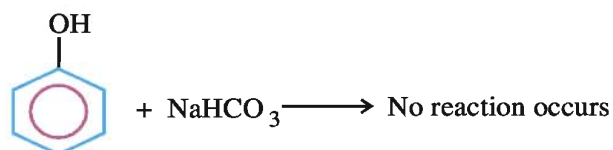
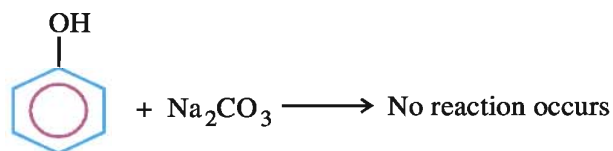
(1) Reactions due to–OH group (2) Reaction occurring in aromatic ring

(1) Reactions due to–OH group :

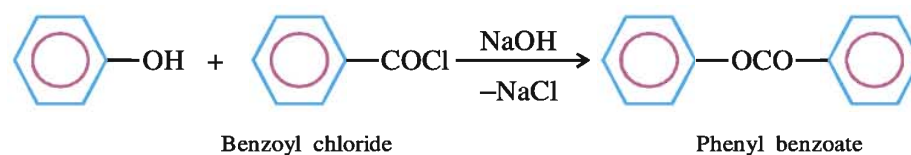
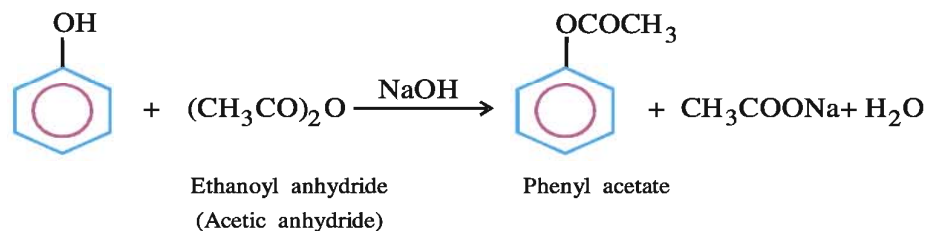
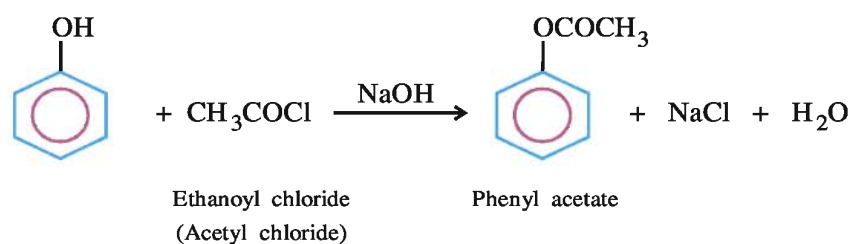
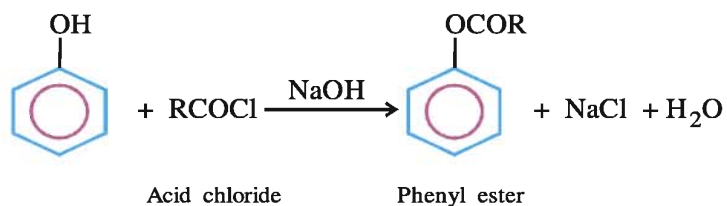
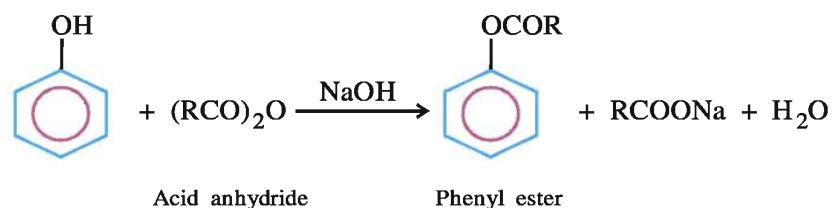
(i) Formation of salt : Reaction of phenol with aqueous sodium hydroxide forms salt and water.



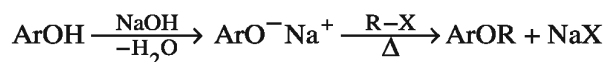
Phenol is weak acid so it does not give reaction with sodium carbonate and sodium hydrogen carbonate.



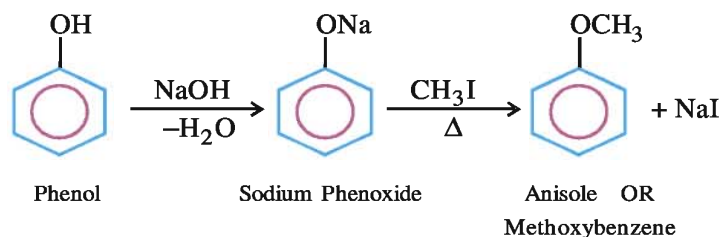
(ii) Formation of phenyl ester : Phenol forms phenyl ester through reaction with acid anhydride or acid chloride in alkaline medium.

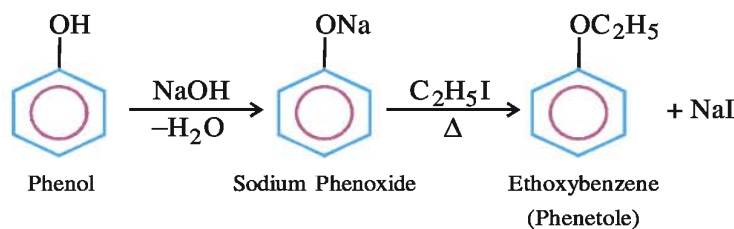


(iii) Formation of aryl ether : Heating the solution of phenol prepared in aqueous solution of sodium hydroxide, after addition of haloalkane it forms ether. This formation reaction of ether is called Williamson synthesis.

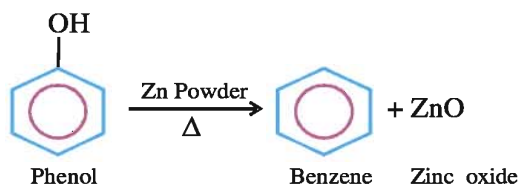


e.g.,





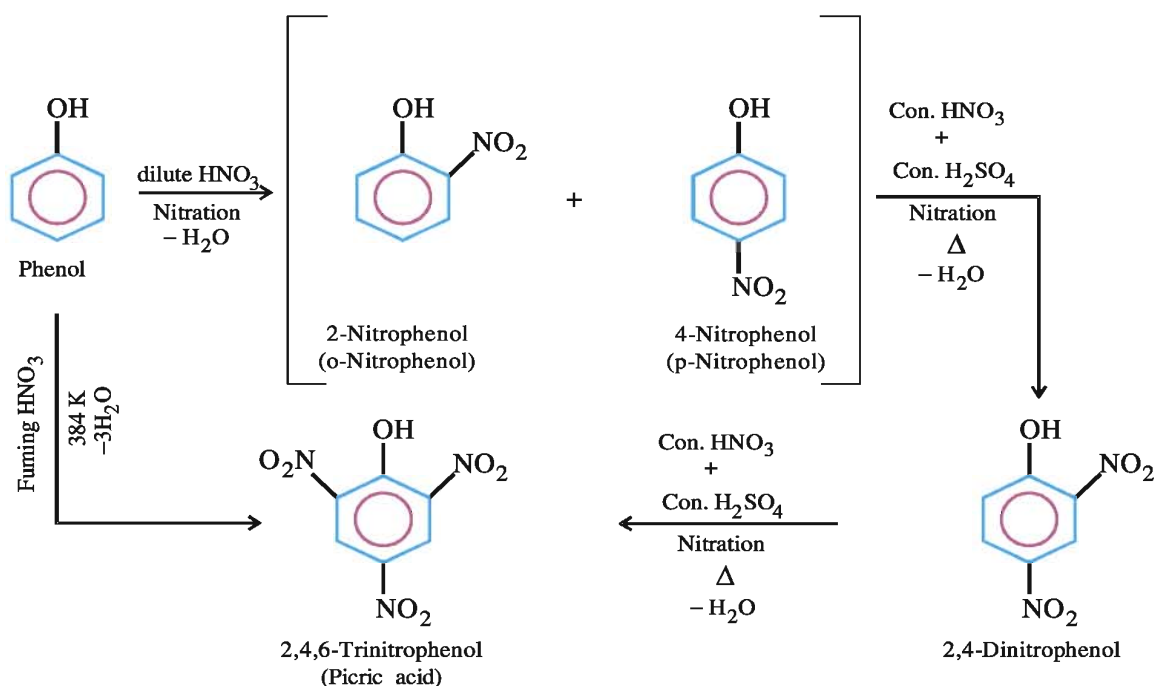
(iv) **Formation of benzene** : The mixture of aqueous phenol and zinc powder is heated. As a result benzene and zinc oxide are formed. In this reaction hydroxyl group attached to aromatic nucleus is eliminated.



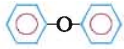

(2) Reactions occurring in aromatic ring :

(i) **Electrophilic substitution reaction** : The hydroxyl group of phenol being ortho-para directing, electrophilic substitution reaction like nitration and bromination of phenol give ortho-para derivatives.

(A) **Nitration of phenol** : The chemical reaction between phenol and dilute nitric acid forms mixture of 2-nitrophenol (ortho-nitrophenol) and 4-nitrophenol (para-nitrophenol). It is called first nitration reaction. Second nitration of it occurs by heating with mixture of concentrated HNO_3 and concentrated H_2SO_4 to form 2,4-dinitrophenol and by third nitration 2,4,6-trinitrophenol (picric acid) is formed. Reaction of phenol with concentrated nitric acid also forms picric acid but product of this reaction is less.



7.13 Nomenclature of Ether Compounds

As we have studied in the beginning of this unit, general formula of ether is $R_1/Ar_1-O-R_2/Ar_2$ where R_1 and R_2 = alkyl or alkenyl or alkynyl group; Ar_1 and Ar_2 = aryl group. If both hydrocarbon groups attached to oxygen of ether compounds are same, then it is called **simple or symmetrical ether**. e.g., CH_3OCH_3 , $C_2H_5OC_2H_5$,  etc. If both hydrocarbon groups attached to oxygen of ether compounds are different then it is called **mixed or unsymmetrical ether**. e.g., $CH_3OCH_2CH_3$, $CH_3OCH_2CH_2CH_3$,  etc.

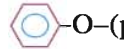




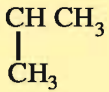
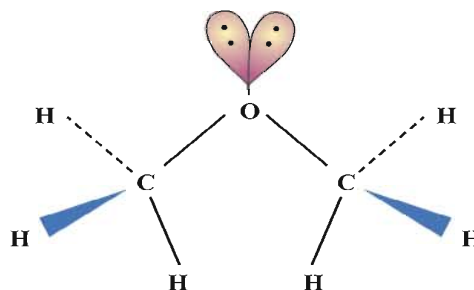
For common name of ethers, the names of two hydrocarbon groups are cited in alphabetical order and the word, 'ether' is added at the end. If both the hydrocarbon groups are the same, the prefix 'di' is added before the name of hydrocarbon group and word 'ether' added at the end (see table 7.5). **In IUPAC nomenclature of ethers, ether is mentioned as substituted hydrocarbon by alkoxy (RO-) or phenoxy (ArO-) group.** Alkoxy or phenoxy groups are named by removing the 'yl' from the end of name of alkyl or phenyl group and adding suffix 'oxy'. e.g., CH_3O -(methoxy), C_2H_5O -(ethoxy), -(phenoxy). Thus, IUPAC name of ether is written by adding the name of substituent alkoxy or phenoxy group as prefix before the name of hydrocarbon containing long chain of carbons attached to the oxygen of ether (see table 7.5).

Table 7.5 Ether compounds

Structural formula	IUPAC name	Common name	Type
CH_3-O-CH_3	Methoxymethane	Dimethyl ether	Symmetrical
$CH_3-O-CH_2CH_3$	Methoxyethane	Ethylmethyl ether	Unsymmetrical
$CH_3CH_2-O-CH_2CH_3$	Ethoxyethane	Diethyl ether	Symmetrical
CH_3O- 	Methoxybenzene or Anisole	Methyl phenyl ether (Anisole)	Unsymmetrical
CH_3CH_2O- 	Ethoxybenzene	Ethylphenyl ether (Phenetole)	Unsymmetrical
 -O- 	Phenoxybenzene	Diphenyl ether	Symmetrical
$H_2C=CHCH_2OCH_3$	3-Methoxy prop-1-ene	Methyl propenyl ether	Unsymmetrical
$HC\equiv CCH_2OCH_3$	3-Methoxy prop-1-yne	Methyl propynyl ether	Symmetrical
$CH_2=CH-O-CH=CH_2$	Ethenoxyethene	Divinyl ether	Symmetrical
CH_3CH_2O 	2-Ethoxypropane	Ethyl isopropyl ether	Unsymmetrical

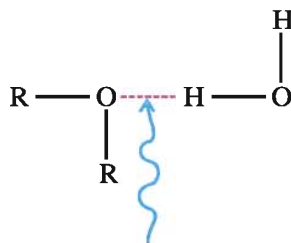
7.14 Electronic Structure of Ether

C-O	σ -bond
C and O	sp^3 hybridisation
C-O-C angle	111.7°



7.15 Physical Properties of Ether

For equal molecular mass containing alcohols and ethers, ethers have lower boiling points than alcohols, because in ethers, intermolecular hydrogen bonds are not present. e.g., Boiling point of methoxy-methane (molecular mass = 46 gram mole⁻¹, b.p. = 248 K) is lower than that of ethanol (molecular mass = 46 gram mole⁻¹, b.p. = 351 K) and boiling point of ethoxyethane (molecular mass = 74 gram mole⁻¹, b.p. = 308 K) is lower than that of butan-1-ol (molecular mass = 74 gram mole⁻¹, b.p. = 390 K). Like alcohol, ether forms intermolecular hydrogen bond with molecule of water. Therefore, solubilities of ethers in water are similar to those of alcohols with the same molecular mass. e.g., same molecular mass containing butan-1-ol and ethoxyethane have solubility in 100 g water is approximately 8 gram.



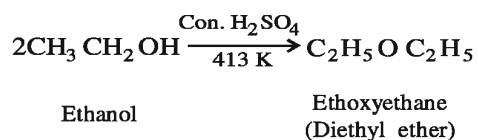
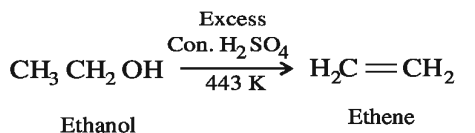
Intermolecular hydrogen bond

Intermolecular hydrogen bond between ether and water molecules

7.16 Preparation of Ethers

Mainly two methods are famous for preparation of ethers :

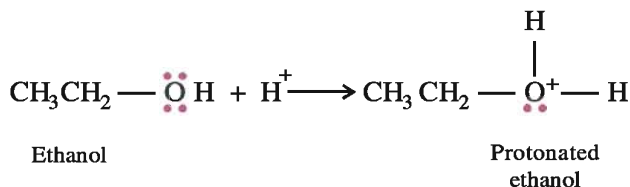
(1) By dehydration of alcohols : Dehydration of alcohols can be possible in presence of acid. Product of this reaction will be either alkene or ether. It depends on the reaction conditions. e.g., Dehydration of ethanol in presence of sulphuric acid gives ethene at 443 K temperature and ethoxyethane at 413 K temperature as a main product.



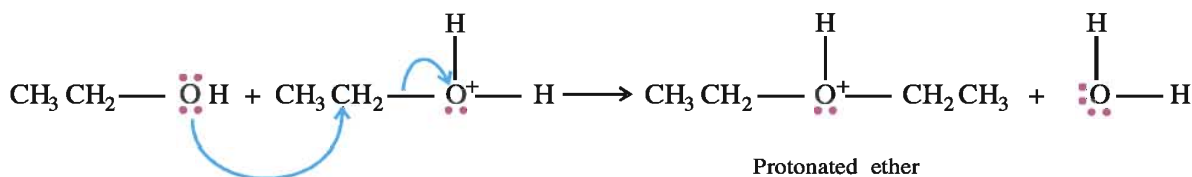
2 moles of ethanol and concentrated sulphuric acid are reacted at 413 K temperature; as a result obtained product ethoxyethane is in vapour form at temperature of reaction due to its lower boiling point 308 K. This vapour when cooled by passing through a water condenser gives liquid ether. In this reaction, if conditions are set in such a way that if ethanol is continuously added from one end so that liquid ethoxyethane is obtained continuously at the other end, the method is known as continuous etherification. Ether is produced industrially by this method.

Mechanism :

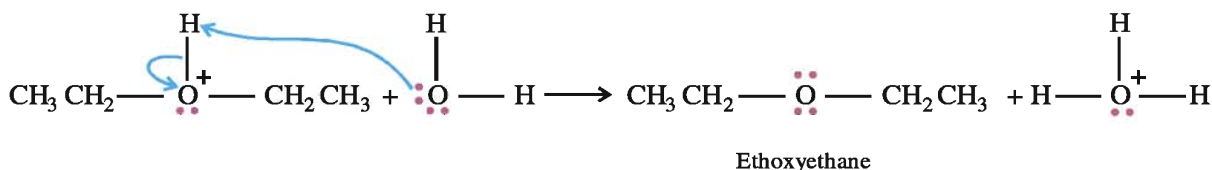
Step-1 : Alcohol accepts proton from the sulphuric acid to form protonated alcohol.



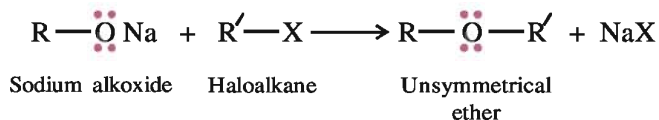
Step-2 : Second molecule of alcohol acts as nucleophilic reagent to attack on protonated alcohol.



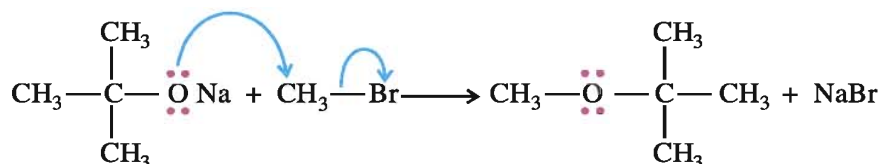
Step-3 : Ether is formed by elimination of proton from the protonated ether.



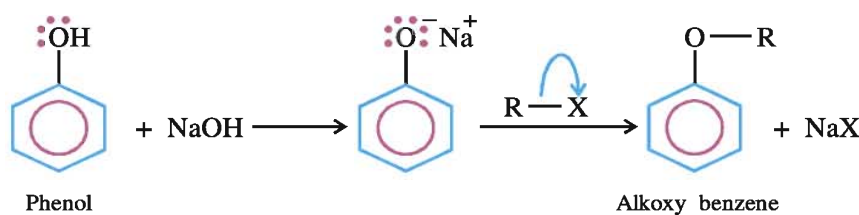
(2) By Williamson synthesis : English Chemist Alexander William Williamson discovered the nucleophilic substitution reaction for synthesis of unsymmetrical ethers. This reaction is called Williamson synthesis. This synthesis is bimolecular nucleophilic substitution (S_{N}^2) reaction of sodium alkoxides and haloalkanes.



If $-\text{R}$ is a secondary or tertiary alkyl group in sodium alkoxide then ether is also synthesised by this reaction.



Only primary haloalkane can synthesise ether easily. If secondary or tertiary haloalkane is used then elimination reaction occurs to form alkene. Therefore ether can be prepared also from phenol.



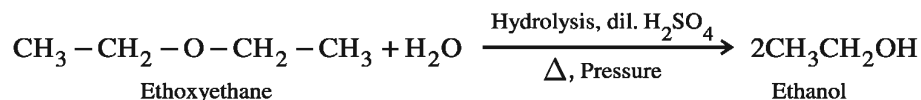
7.17 Chemical Reactions of Ether

Ether compounds having less chemical reactivity, they do not undergo oxidation and reduction. Moreover they do not react with active metals and base. However it gives some reactions with strong acids. Generally two types of reactions occur in ethers :

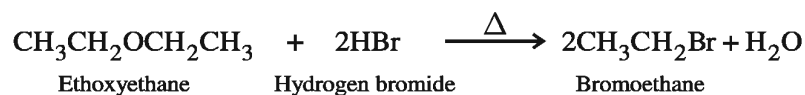
- (1) Reactions involving cleavage of C–O bond.
- (2) Electrophilic substitution reaction occurring in aromatic ring.

(1) Reactions involving cleavage of C–O bond :

(i) Reaction with dilute acid : A mixture of ethoxyethane (diethyl ether) and dilute sulphuric acid is heated in closed vessel under pressure; as a result two moles of ethanol are produced by hydrolysis.

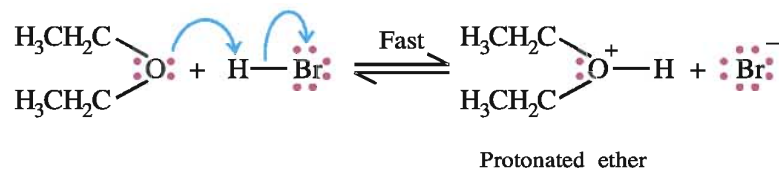


(ii) Reaction with hydrogen halide : If a mixture of ethoxyethane and two moles of concentrated hydro bromide is heated at high temperature, two moles of bromoethane are produced.

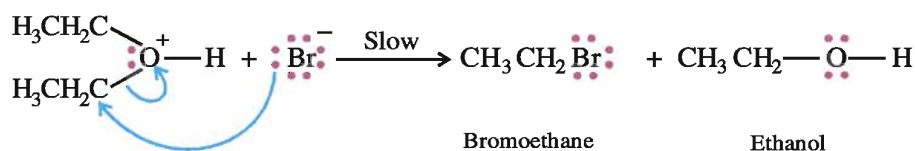


Mechanism :

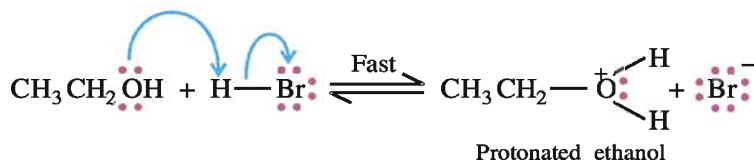
Step-1 : Ethoxyethane is converted to protonated ether by accepting H^+ from hydrogen bromide.



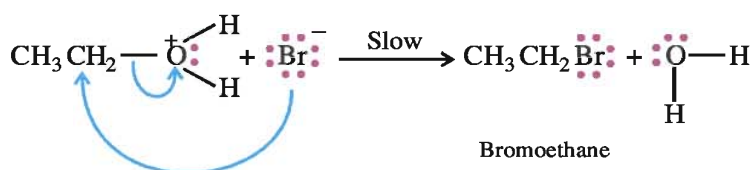
Step-2 : Bromide ion acts as nucleophilic reagent to attack on carbon of protonated ether. During this step one mole bromoethane (ethylbromide) and one mole of ethanol are formed.



Step-3 : Ethanol is converted to protonated ethanol by accepting proton from hydrogen bromide.

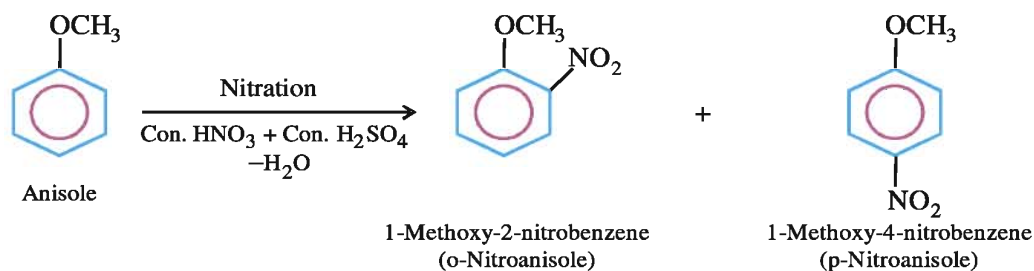


Step-4 : Bromide ion acts as nucleophilic reagent to attack on carbon of protonated ethanol. During this step bromoethane and water are formed.

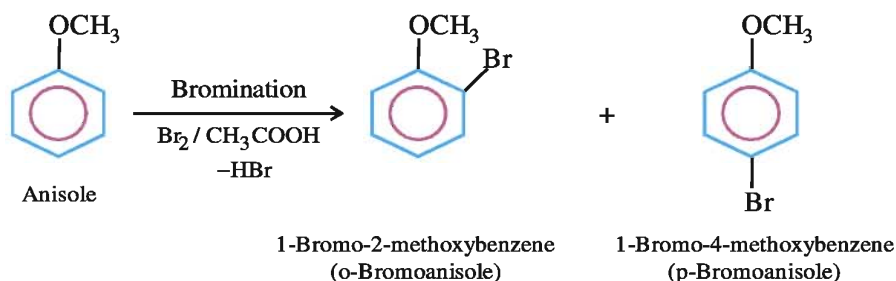


(2) Electrophilic substitution reaction occurring in aromatic ring : The -OR group of alkoxyarene (alkyl aryl ether) compounds being ortho-para directing, their electrophilic substitution reactions give mixture of ortho-para products. These reactions will be understood by following example of anisole.

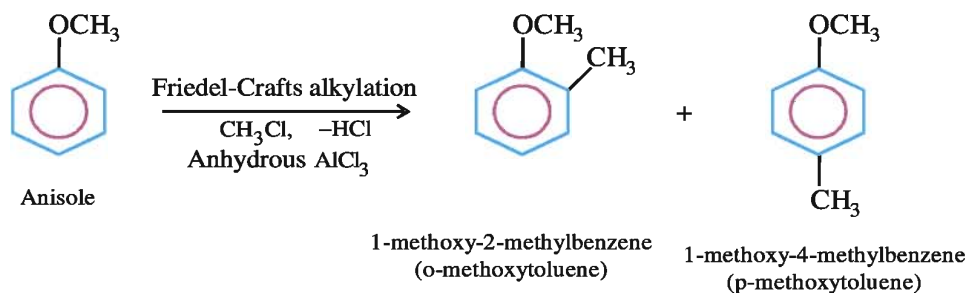
(i) Nitration : Nitration reaction of anisole with mixture of concentrated nitric acid and concentrated sulphuric acid gives mixture of 1-methoxy-2-nitrobenzene (o-nitroanisole) and 1-methoxy-4-nitrobenzene (p-nitroanisole).



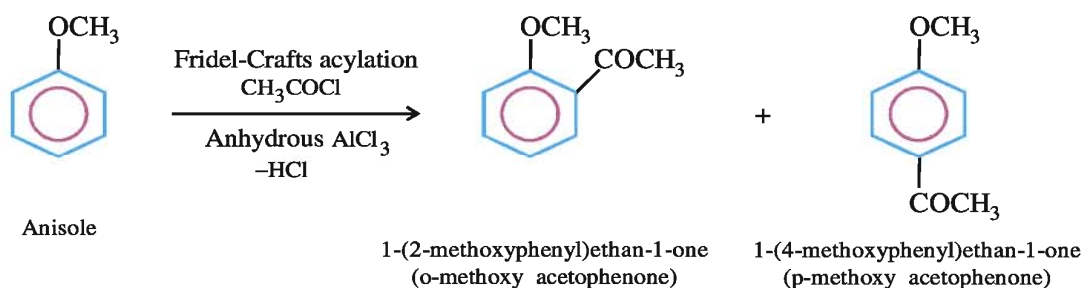
(ii) Bromination : Bromination reaction of anisole with bromine in acetic acid gives 1-bromo-2-methoxybenzene (o-bromoanisole) and 1-bromo-4-methoxybenzene (p-bromoanisole).



(iii) **Friedel-Crafts alkylation** : Friedel-Crafts alkylation reaction of anisole with chloromethane (Methyl chloride) in presence of anhydrous aluminium chloride gives 1-methoxy-2-methylbenzene (o-methoxytoluene) and 1-methoxy-4-methylbenzene (p-methoxytoluene).

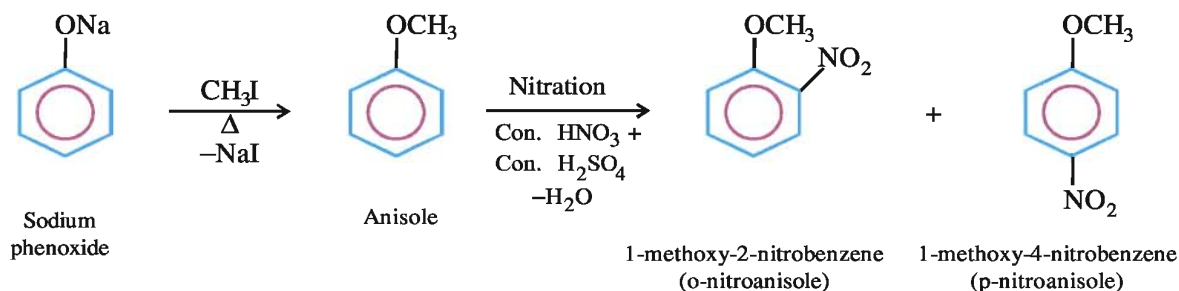


(iv) **Friedel-Crafts acylation** : Friedel-Crafts acylation reaction of anisole with ethanoyl chloride (acetyl chloride) in presence of anhydrous aluminium chloride gives 1-(2-methoxy phenyl) ethan-1-one (o-methoxy acetophenone) and 1-(4-methoxy phenyl) ethan-1-one (p-methoxy acetophenone).

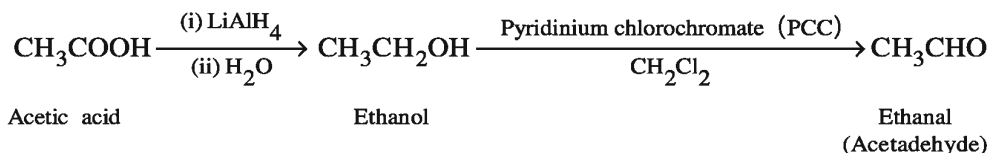


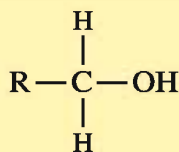
Some organic conversions :

(1) **1-Methoxy-2-nitrobenzene and 1-methoxy-4-nitrobenzene from sodium phenoxide**

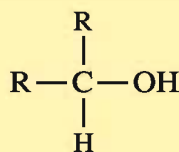


(2) **Ethanal (acetaldehyde) from acetic acid**

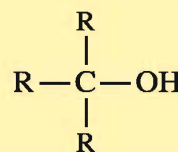




Primary (1^o) alcohol



Secondary (2^o) alcohol



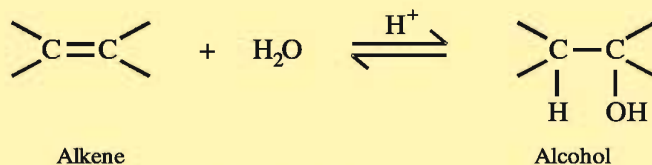
Tertiary (3^o) alcohol

Physical Properties of Alcohols : The boiling points of alcohols are higher than those of alkanes having approximately equal molecular mass. In linear series of primary alcohols, the boiling point increases gradually as the number of carbon atoms increases. Among alcohols containing same molecular formula, secondary alcohol has lower boiling point than primary alcohol and tertiary alcohol has lower boiling point than secondary alcohol. In alcohol molecules, increase in the boiling point and solubility in water will increase with increase in number of hydroxyl groups.

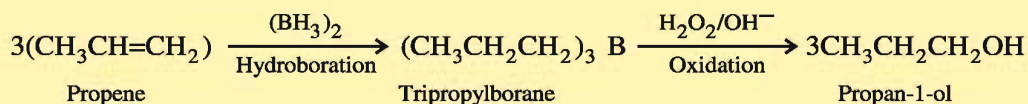
Preparation of Alcohols :

(1) Alcohol from alkene compounds

(i) By acid catalysed hydration

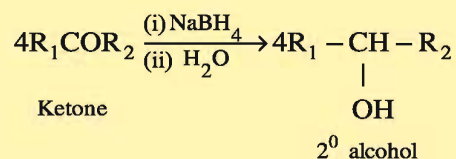
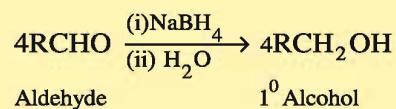


(ii) By hydroboration-oxidation

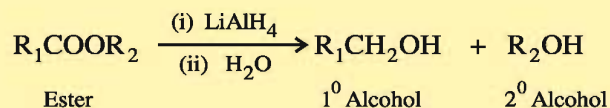
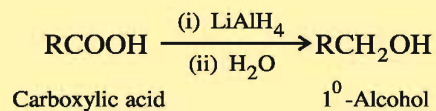


(2) Alcohols from carbonyl compounds

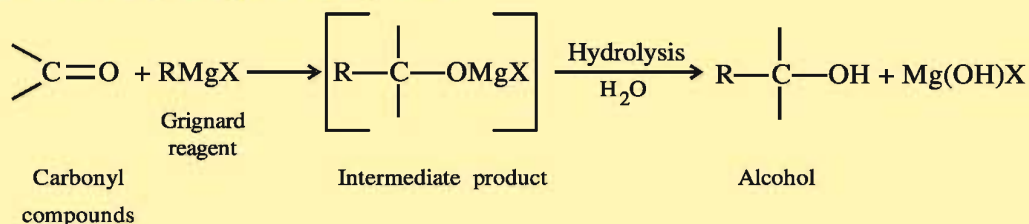
(i) By reduction of aldehydes and ketones



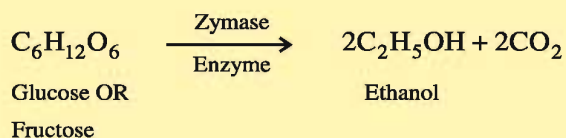
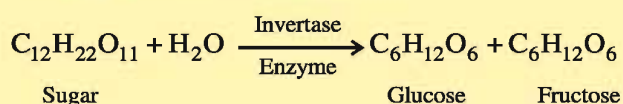
(ii) By reduction of carboxylic acids or esters



(3) Alcohols by Grignard reagents



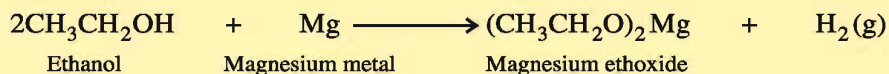
(4) By fermentation method



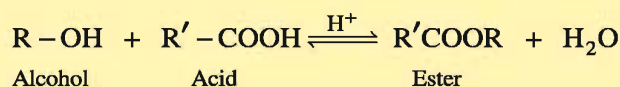
Chemical Reactions of Alcohols :

(1) Reactions involving cleavage of O-H group

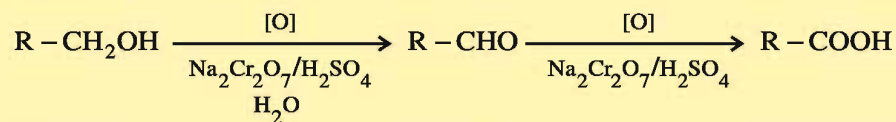
(i) Reaction of alcohol with active metals



(ii) Reaction with acids



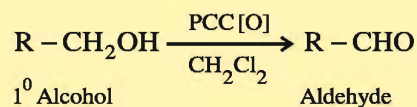
(iii) Oxidation of alcohols



1^o Alcohol

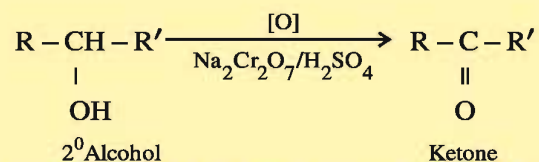
Aldehyde

Carboxylic acid



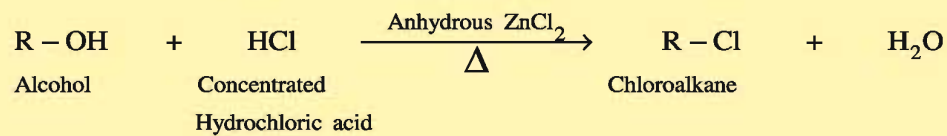
1^o Alcohol

Aldehyde

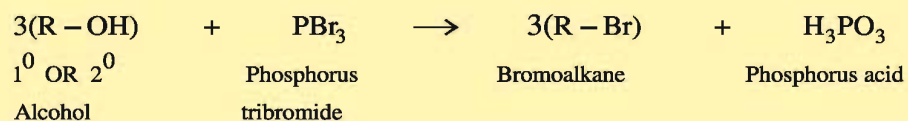


(2) Reactions involving cleavage of C-O bond

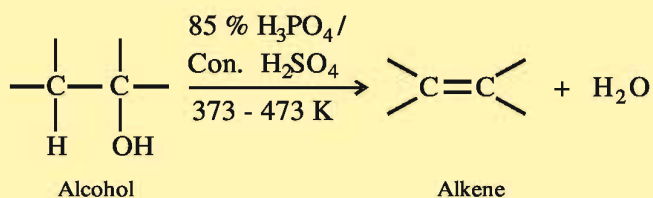
(i) Reaction with halogen acid (Lucas test)



(ii) Reaction with phosphorus tribromide



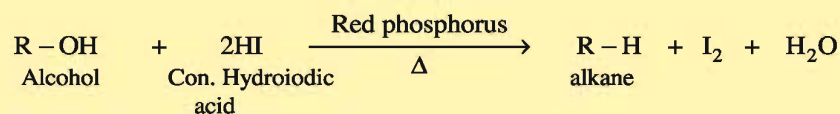
(iii) Dehydration of alcohols



The order of ease of dehydration reaction of alcohols is

3^o alcohol > 2^o alcohol > 1^o alcohol

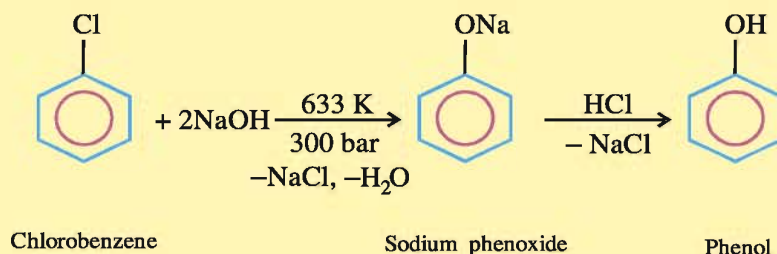
(iv) Reduction of alcohol



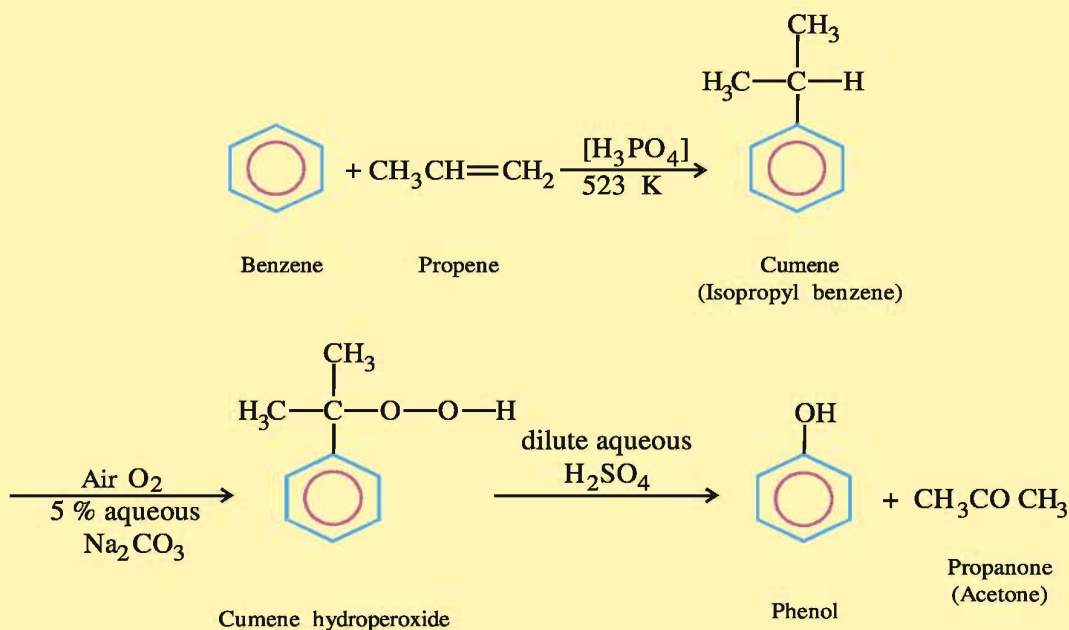
Physical Properties of Phenol : Phenol has higher boiling point and solubility in water than toluene (arene compounds) and fluorobenzene (halo arene compounds) having approximately same molecular mass. Some ortho substituted phenols like o-nitrophenol has lower melting point and less solubility in water than its m- and p- isomers. Aqueous solution of phenol shows acidic nature.

Preparation of phenol :

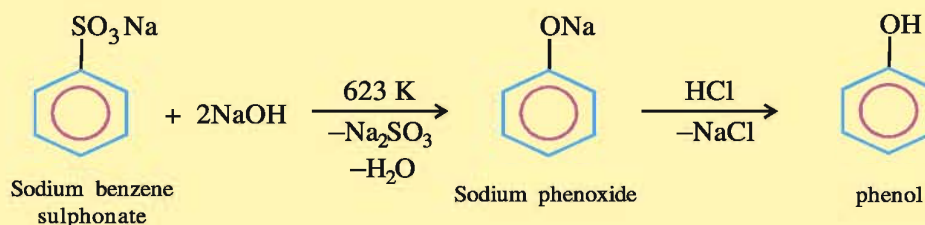
(1) Dow process



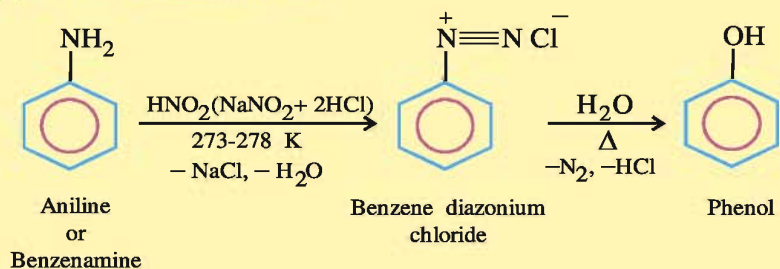
(2) Cumene process



(3) From sodium benzene sulphonate



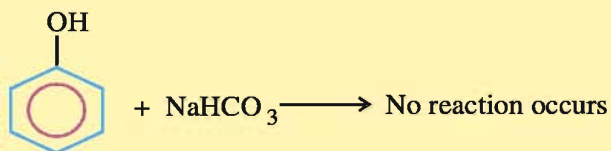
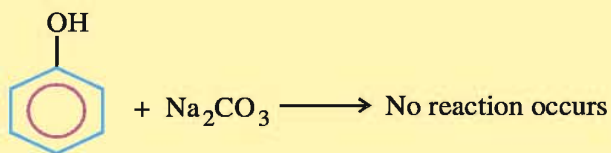
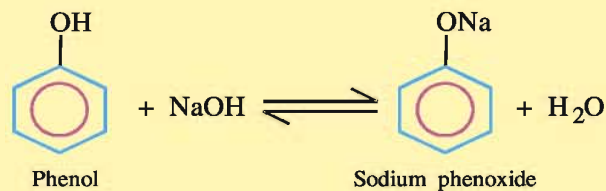
(4) From diazonium salt



Chemical Reactions of phenol :

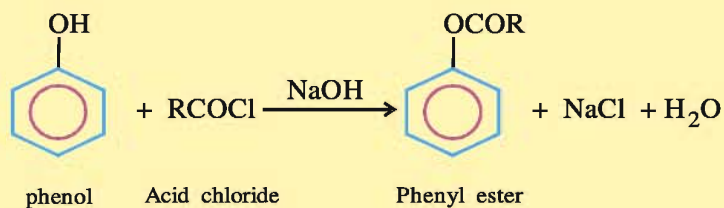
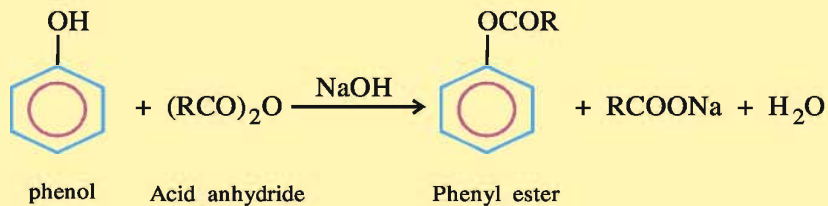
(1) Reactions due to $-\text{OH}$ group

(i) Formation of salt

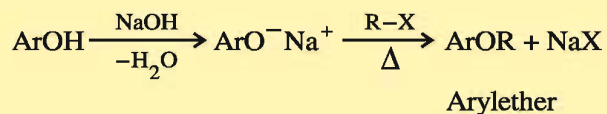


Thus, the nature of phenol is like weak acid.

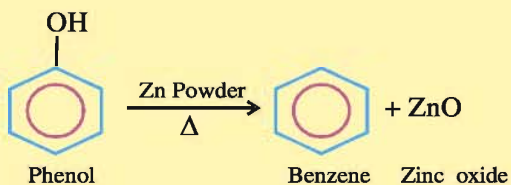
(ii) Formation of phenyl ester



(iii) Formation of aryl ether



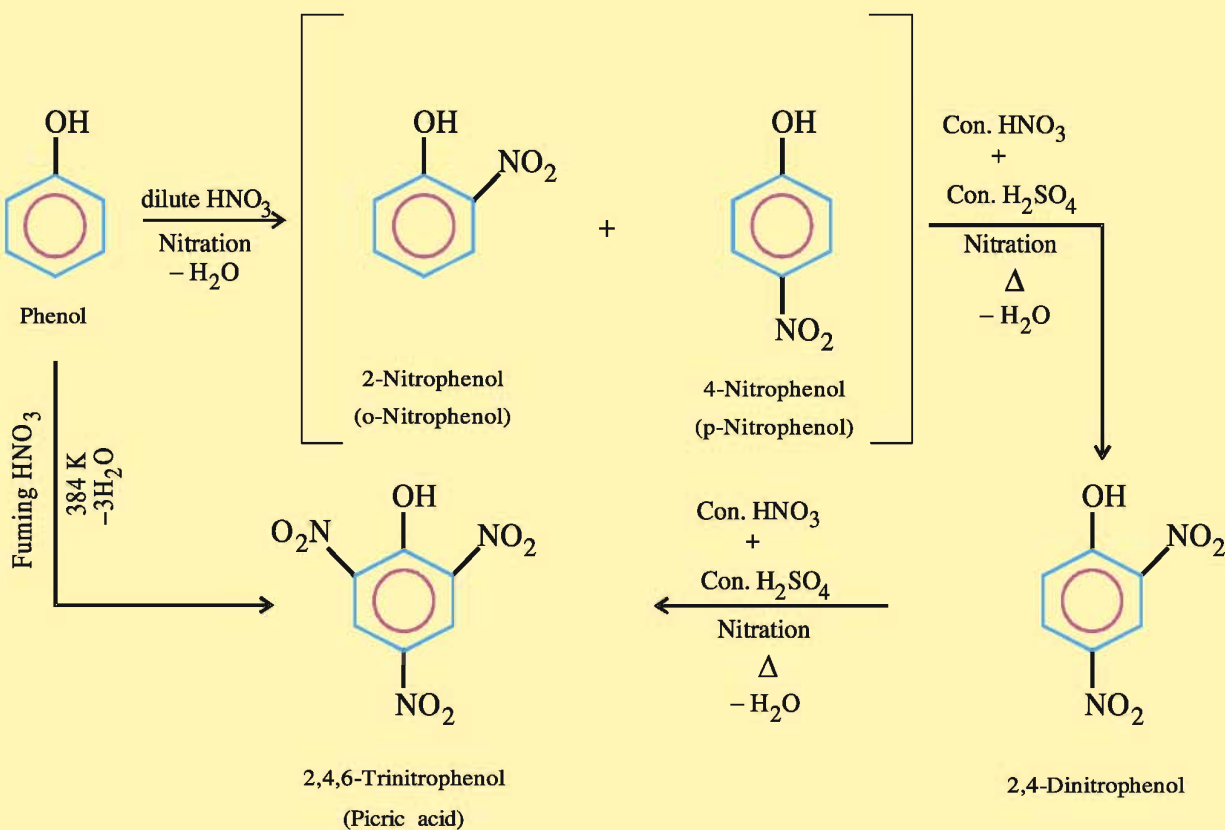
(iv) Formation of benzene



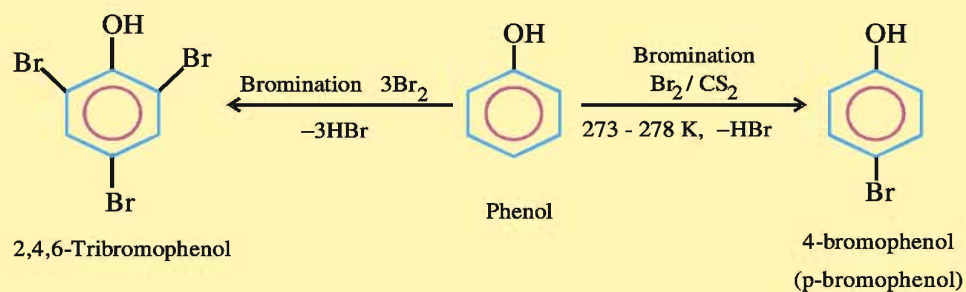
(2) Reactions occurring in aromatic ring

(i) Electrophilic substitution reaction

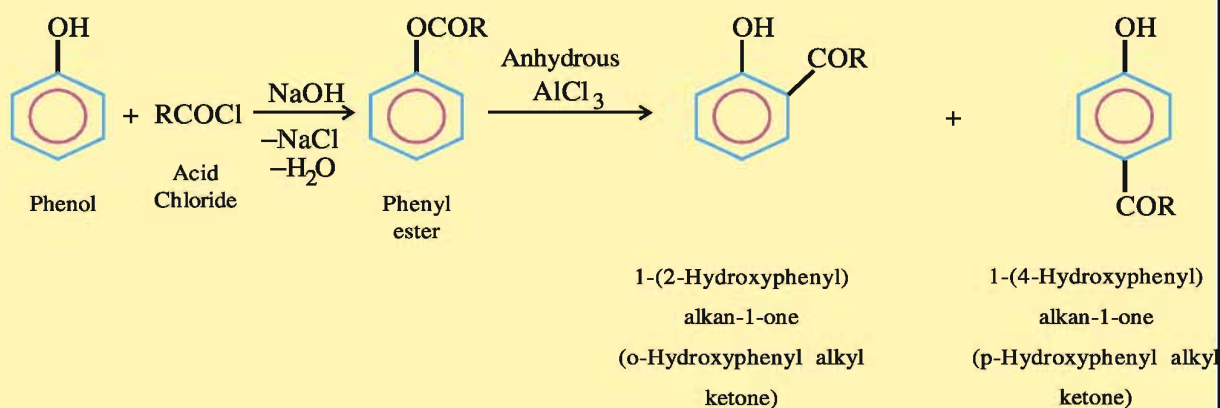
(A) Nitration of phenol



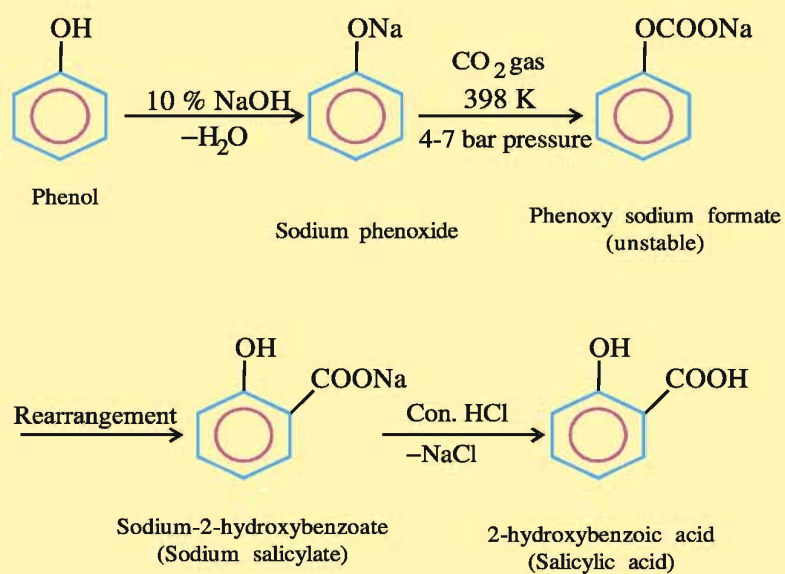
(B) Bromination of phenol



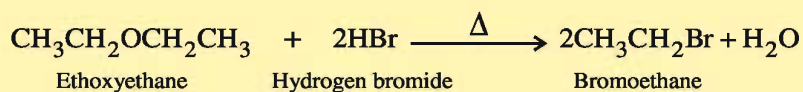
(ii) Fries Rearrangement



(iii) Kolbe-Schmitt Reaction

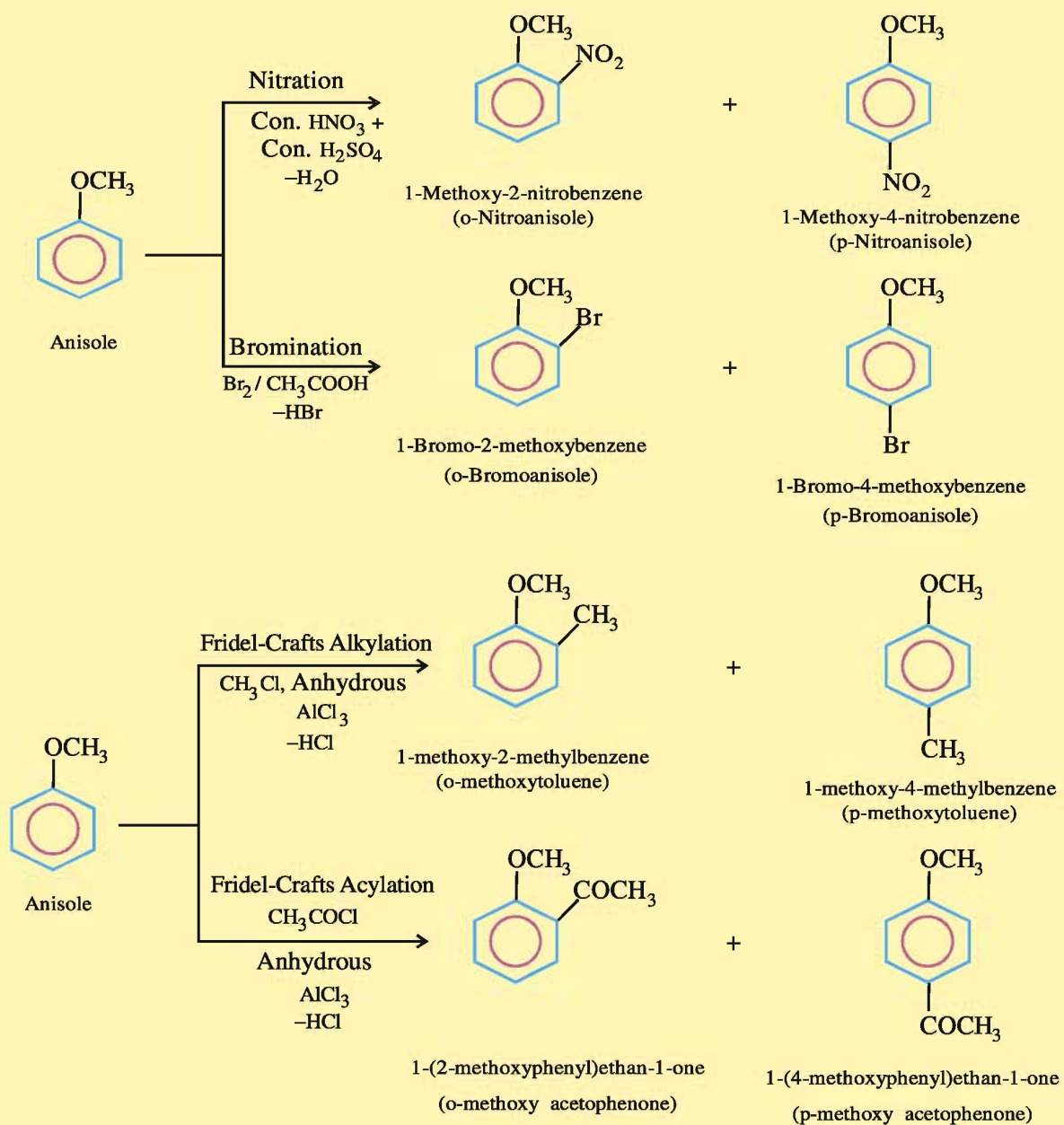


(ii) Reaction with hydrogen halide



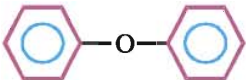
(2) Electrophilic substitution reaction occurring in aromatic ring

The -OR group of alkyaryl ether compounds being ortho-para directing, their electrophilic substitution reactions give mixture of ortho-para products.

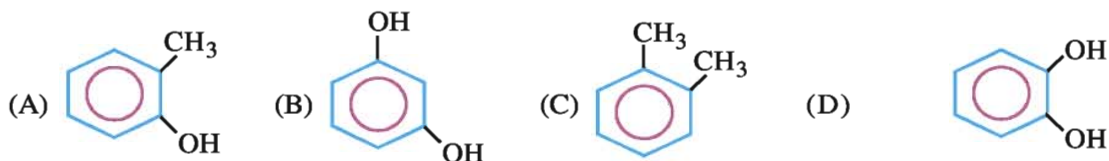


EXERCISES

1. Select the proper choice from the given multiple choices :

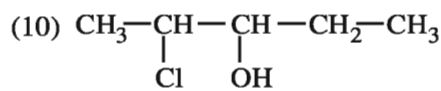
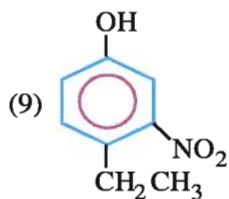
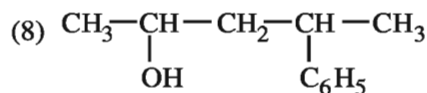
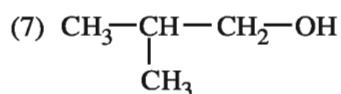
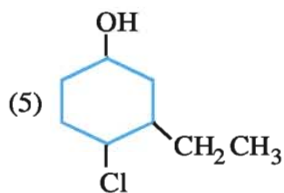
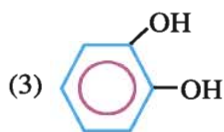
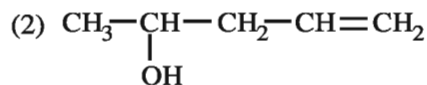
- (1) Which general formula is that of alcohol ?
(A) R_1-O-R_2 (B) $Ar-OH$ (C) $R-OH$ (D) Ar_1-O-Ar_2
- (2) Which formula is of tertiary alcohol ?
(A) CH_3OH (B) $(CH_3)_2CHOH$ (C) $(CH_3)_3COH$ (D) CH_3CH_2OH
- (3) Which order from the following is true for boiling points ?
(A) Chloroethane < ethane < ethanol (B) Ethane < chloroethane < ethanol
(C) Ethanol < ethane < chloroethane (D) Ethane > chloroethane > ethanol
- (4) Which substance from the following is a reducing agent ?
(A) Potassium permanganate (B) Lithium aluminium hydride
(C) Chromic acid (D) Pyridinium chloro chromate
- (5) Which substance from the following is unsymmetrical ether ?
(A)  (B) $C_2H_5-O-CH_2CH_3$
(C) $CH_3-O-C_2H_5$ (D) CH_3-O-CH_3
- (6) What will be formed after oxidation reaction of 2^o alcohol with chromic acid ?
(A) Aldehyde (B) Ketone (C) Carboxylic acid (D) Ester
- (7) In which from the following intermolecular hydrogen bond is not present ?
(A) alcohol-alcohol (B) alcohol-water (C) ether-ether (D) ether-water
- (8) Which species from the following is nucleophilic reagent ?
(A) E (B) E^+ (C) E^- (D) $\overset{\cdot}{E}$
- (9) Which statement from the following is true ?
(A) During dehydration reaction H_2O molecule is added to reactant
(B) Lucas test is used for detection of ethers
(C) During esterification OH^- from acid molecule and H^+ from alcohol are removed.
(D) During esterification H^+ from acid molecule and OH^- from alcohol are removed.

(10) Which structural formula is of o-cresol ?



2. Answer the following question in short :

(A) Write IUPAC name of the following compounds :



(B) Mention the structures of the following IUPAC named compounds :

(1) 1-Ethoxy-3-methylpentane

(2) 2-Chloropentan-3-ol

(3) 3-Bromophenol

(4) 2-Nitrophenol

(5) Cyclohexane-1,2-diol

(6) 2-Isopropoxypentane

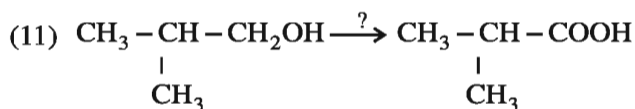
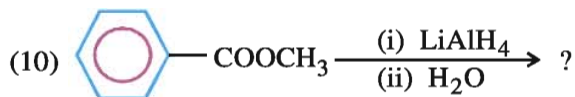
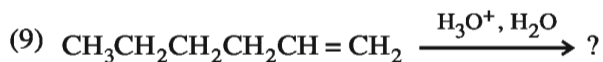
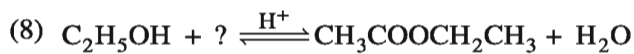
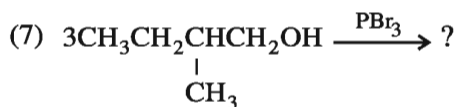
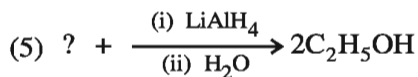
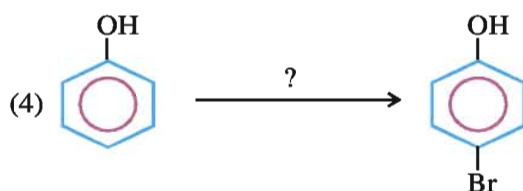
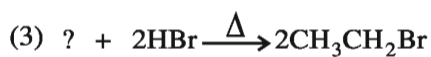
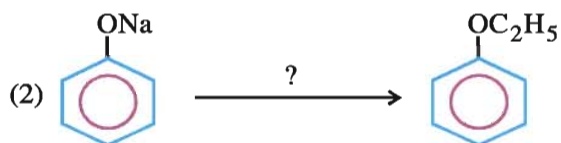
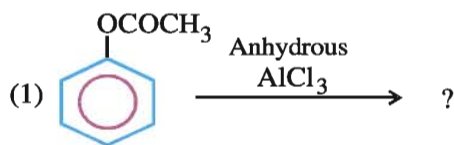
(7) 2,2-Dimethylpropan-1-ol

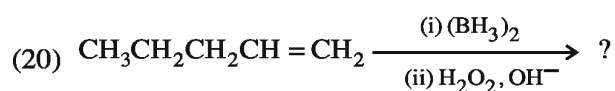
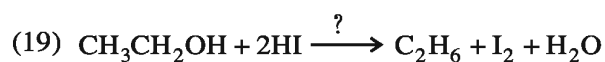
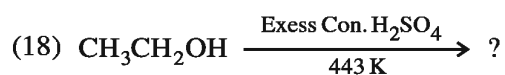
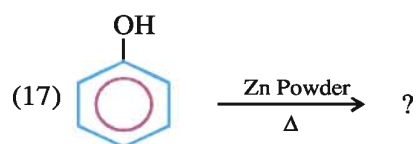
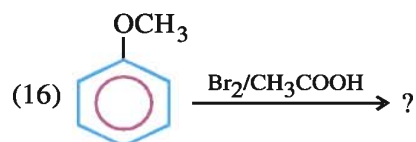
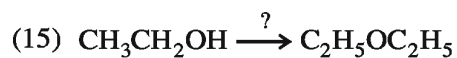
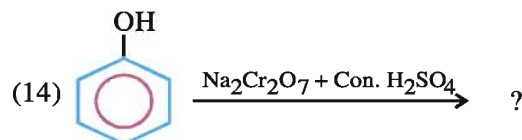
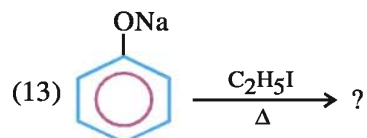
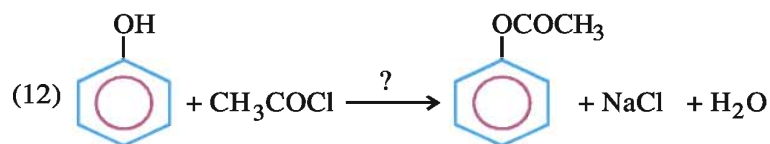
(8) 2,4-Dimethylpentan-1-ol

(9) 2,6-Dimethylphenol

(10) 1,2-Dimethoxyethane

(C) Complete the following chemical reactions :





3. Answer the following questions :

(A) Explain the following statements giving scientific reasons with example :

- (1) The boiling points of alcohols are higher than those of alkanes having equal molecular masses.
- (2) While going from primary to tertiary isomeric alcohols, their boiling points are decreasing.
- (3) Phenol has higher boiling point than toluene and fluorobenzene having approximately same molecular mass.

- (4) o-Nitrophenol has lower melting point and solubility in water than m- and p-nitrophenol.
- (5) Aqueous solution of phenol is more acidic than alcohol.
- (6) Ethers have lower boiling point than alcohols having same molecular mass.

(B) Write equation of chemical conversions for following organic compounds :

- (1) Acetone from propene
- (2) Propan-1-ol from propene
- (3) Hexan-2-ol from hex-1-ene
- (4) Butan-2-ol from acetaldehyde
- (5) Phenol from chlorobenzene
- (6) Phenol from aniline
- (7) Ethoxybenzene from phenol
- (8) 2, 4-Dinitro phenol from phenol
- (9) 2-Hydroxy benzoic acid from phenol
- (10) 2-Hydroxy benzaldehyde from phenol
- (11) 1-Methoxy-2-methylbenzene and 1-methoxy-4-methylbenzene from sodium phenoxide.
- (12) 1-(2-Hydroxyphenyl) propan-1-one and 1-(4-Hydroxyphenyl) propan-1-one from phenol

(C) Write chemical equations for the following reactions :

- (1) Oxidation reactions of primary, secondary and tertiary alcohols.
- (2) Reactions of ethanol with (i) Mg (ii) CH_3COOH (iii) PBr_3 (iv) HI.
- (3) Reactions of preparation for (i) phenyl acetate (ii) anisole (iii) benzene from phenol
- (4) Nitration and bromination reactions of phenol
- (5) Reactions of ethoxyethane with
 - (i) dilute H_2SO_4
 - (ii) concentrated HBr.
- (6) Nitration and bromination reactions of anisole.
- (7) Friedel-Crafts alkylation and acylation reactions of anisole

4. Answer the following questions in detail :

(A) Explain the following reactions with mechanism :

- (1) Preparation of alcohols from alkene compounds by acid catalysed hydration.
- (2) Preparation of alcohols from alkene compounds by hydroboration-oxidation.
- (3) Preparation of alcohols by reduction of aldehydes and ketones.
- (4) Preparation of alcohols from carbonyl compounds by Grignard reagent.
- (5) Reaction of tertiary alcohol with hydrochloric acid.
- (6) Reaction of alcohol with phosphorus tribromide.
- (7) Preparation of ethene by dehydration reaction of ethanol.
- (8) Preparation of ethers by dehydration reaction of alcohols.
- (9) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + 2\text{HBr} \xrightarrow{\Delta} 2\text{CH}_3\text{CH}_2\text{Br} + \text{H}_2\text{O}$

(B) Write short notes on following :

- (1) Preparation of alcohols by fermentation method
- (2) Industrial production of phenol by Dow process and Cumene process
- (3) Lucas test
- (4) Fries rearrangement
- (5) Kolbe-Schmitt reaction
- (6) Reimer-Tiemann reaction
- (7) Williamson synthesis
- (8) Classification of alcohols and ethers

