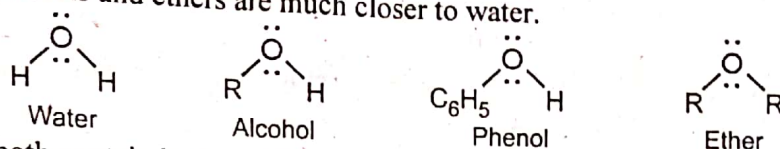


CHAPTER 18

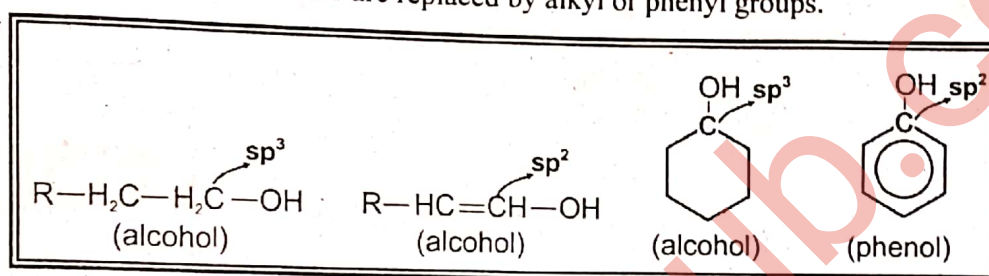
ALCOHOLS, PHENOLS AND ETHERS

Introduction

The structure of alcohols, phenols and ethers are much closer to water.



- Alcohols and phenols both contain hydroxyl ($-OH$) group attached to alkyl and phenyl groups, respectively.
- In ether, both hydrogen atoms of water are replaced by alkyl or phenyl groups.



ALCOHOLS

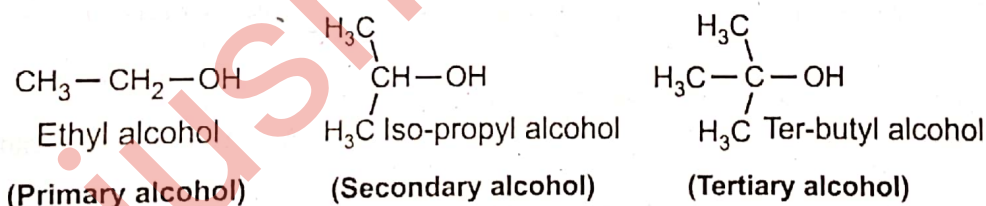
The aliphatic organic compounds containing hydroxyl group $-OH$, as functional group are called alcohols. Alcohols containing one $-OH$ group are called monohydric alcohols and those containing two or more hydroxyl groups are known as polyhydric alcohol.

Classification of Monohydric Alcohols

Monohydric alcohols are classified into the following three families:

- (i) Primary alcohols (ii) Secondary alcohols (iii) Tertiary alcohols

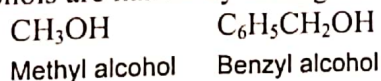
Examples:



Nomenclature

1. Common System of Naming

In common system alcohols are named by adding the word alcohol after the name of the alkyl group to which the $-OH$ group is attached. e.g.

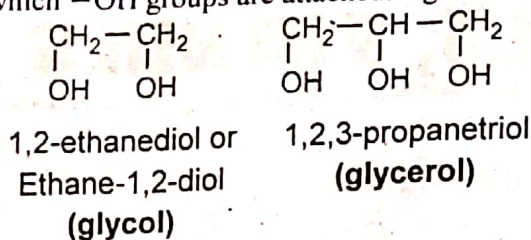


2. IUPAC System

According to this system

- The longest chain of carbon atoms containing the hydroxyl group is selected as the parent hydrocarbon.
- The ending 'e' of the parent hydrocarbon is replaced by 'ol'.
- The carbon chain bearing $-OH$ group is numbered, beginning from that end which would assign the lowest possible number to carbon atom linked to the $-OH$ group.

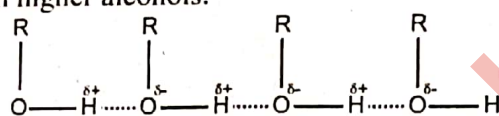
- (iv) The position of $-OH$ group is indicated by placing the number of carbon to which $-OH$ is attached before the name of alcohol.
- (v) The presence of more than one $-OH$ groups is indicated by suffixes $-diol$, $-triol$, etc. and repeating the number of carbon atoms on which $-OH$ groups are attached. e.g.



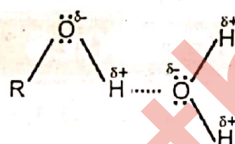
- (vi) In unsaturated alcohol, the hydroxyl group gets the lower number rather than unsaturation, e.g.,
- $$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{OH}$$
- 2-Butene-1-ol

Physical Properties

- Alcohols upto butanol are generally colorless liquids with characteristic sweet smell and burning taste.
- They are readily soluble in water. The solubility of alcohols is due to hydrogen bonding which is significant in lower alcohols but decreases in higher alcohols.



Hydrogen bonding in alcohol



Hydrogen bonding between water and alcohol

Compound	Melting Point ($^{\circ}\text{C}$)	Boiling Point ($^{\circ}\text{C}$)
CH_3OH	-97.8	65.0
$\text{CH}_3\text{CH}_2\text{OH}$	-114.7	78.5
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	-126.5	97.4
$\text{CH}_3(\text{CH}_2)_3\text{OH}$	-89.5	117.3
$\text{CH}_3(\text{CH}_2)_4\text{OH}$	-79.0	138

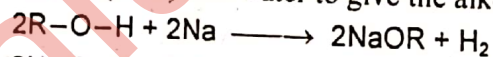
- Melting and boiling points of alcohols are higher than corresponding alkanes. This is due to hydrogen bonding which is present in alcohols but absent in alkanes.

Structure

- The alcohol functional group consists of an O atom bonded to a C atom and a H atom via σ -bonds.
- Both the C-O and the O-H bonds are polar due to the high electronegativity of the O atom.

Acidity

- Due to the high electronegativity of the O atoms, alcohols are slightly acidic.
- The anion derived by the deprotonation of an alcohol is the alkoxide. Alkoxides are important bases in organic chemistry.
- Alcohols react with Na (or K) like water to give the alkoxide:



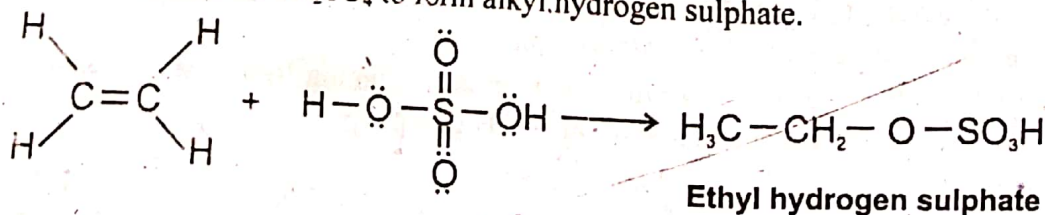
Preparations of Alcohols

1) Hydration of Alkenes

Hydration of alkenes is carried out in the following two steps:

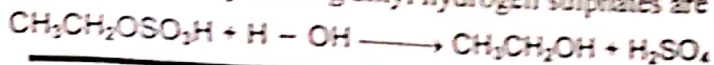
(a) Preparation of alkyl hydrogen sulphate:

Alkenes are dissolved in concentrated H_2SO_4 to form alkyl hydrogen sulphate.

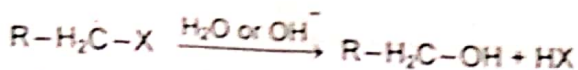


(b) Hydrolysis of alkyl hydrogen sulphate:

On dilution with water followed by heating alkyl hydrogen sulphates are hydrolyzed to alcohols.



(2) Hydrolysis of Alkyl halides

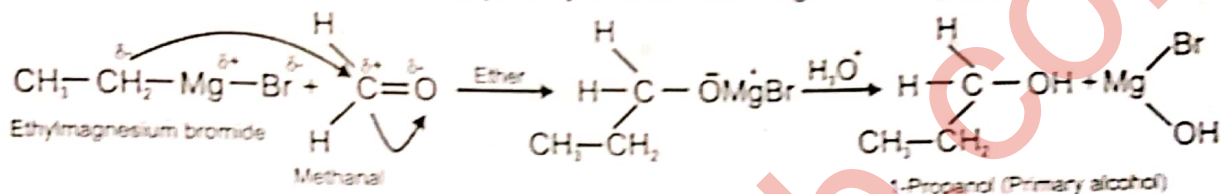


- Alkyl halides can be converted to alcohols using water or hydroxide as the nucleophile.
- Mechanism is a simple nucleophilic substitution

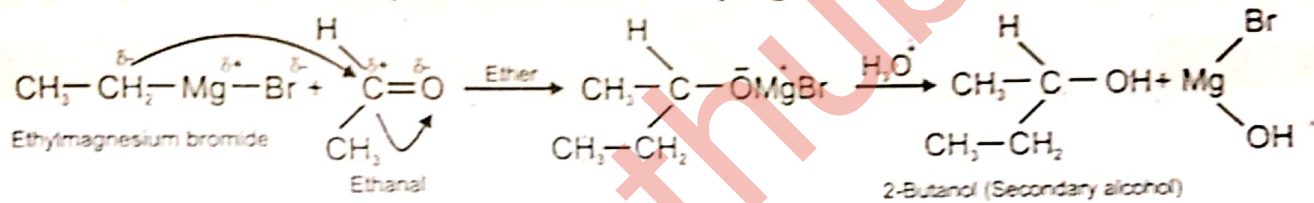
(3) Reactions of RLi or RMgX with Aldehydes and Ketones

Primary, secondary and tertiary alcohols can be prepared by the use of Grignard's reagent (RMgX). The Grignard's reagent adds to a carbonyl molecule and the resulting compounds forms alcohol on hydrolysis.

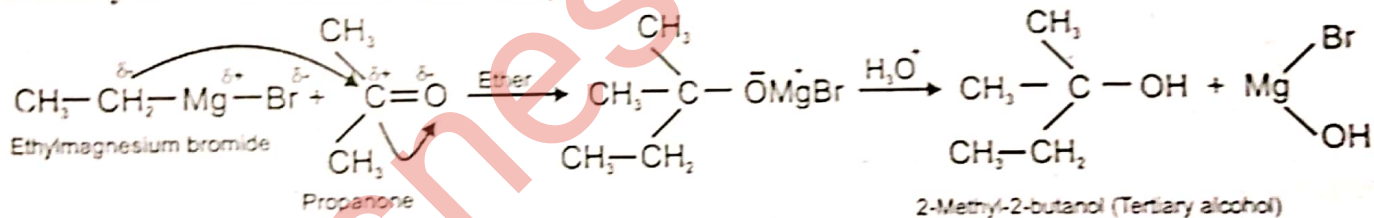
(a) Primary alcohol: Formaldehyde gives primary alcohol with Grignard's reagent:



(b) Secondary Alcohols: Aldehydes other than formaldehyde give secondary alcohols e.g.

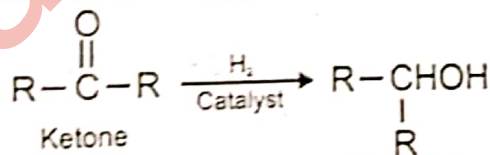


(c) Tertiary Alcohols: Ketones form tertiary alcohols with Grignard's reagent under similar conditions e.g.



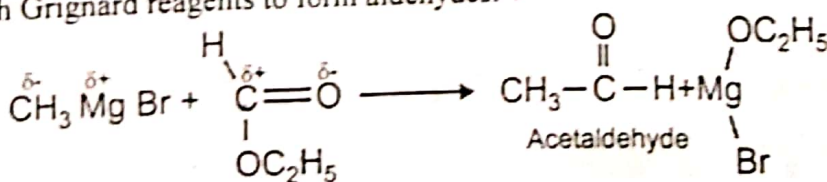
(4) Reduction of Aldehydes and Ketones

Reduction of aldehydes, ketones and carboxylic acid (esters in the presence of Ni, Pd or Pt) gives alcohols e.g.



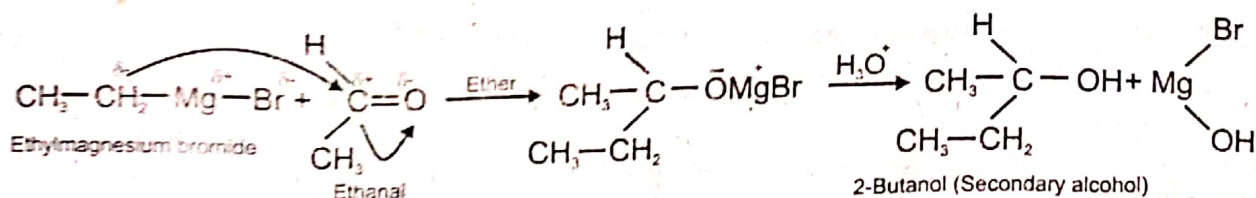
(5) Reactions of RLi or RMgX with Esters

Esters react with Grignard reagents to form aldehydes.



Ethyl formate

The aldehyde so formed reacts with another molecule of Grignard's reagent to give alcohol.



Similarly other esters give secondary and tertiary alcohols with Grignard's Reagents.

(6) Reduction of Carboxylic acids and Esters

LiAlH_4 besides reducing aldehydes and ketones, also reduces carboxylic acids and esters to give alcohols.



Elaboration

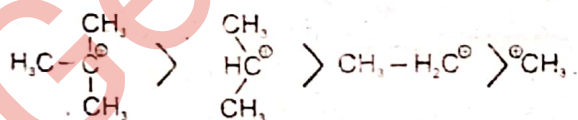
- Carboxylic acids and esters are less reactive to Nu than aldehydes or ketones.
- As a result they can only be reduced by LiAlH_4 and NOT by the less reactive NaBH_4 .
- Each reaction requires that 2 hydrides be added to the carbonyl carbon of acids or esters.

Reactivity

Alcohols react with other reagents in two ways:

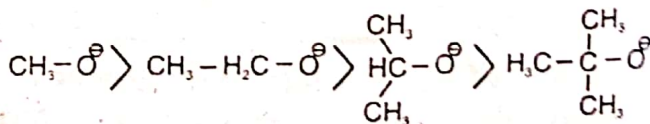
Reaction in which C-O bond breaks (S_N Reactions)	Reaction in which O-H bond breaks (ES Reactions)
<ul style="list-style-type: none"> If a nucleophile attacks on an alcohol, it is the C-O bond which breaks. As a result a carbocation is formed. $ \text{CH}_3-\overset{\delta+}{\text{C}}\overset{\delta-}{\text{H}}\text{OH} \xrightarrow{\text{Nucleophile}} \text{CH}_3-\overset{\delta+}{\text{C}}\overset{\delta-}{\text{H}} + \text{OH}^- $	<ul style="list-style-type: none"> If an electrophile attacks on an alcohol, it is the O-H bond which breaks. $ \text{CH}_3-\overset{\delta-}{\text{C}}\overset{\delta+}{\text{H}}-\text{O}-\text{H} \xrightarrow{\text{Electrophile}} \text{CH}_3-\overset{\delta-}{\text{C}}\overset{\delta+}{\text{H}}-\text{O}^+ + \text{H}^- $
Order of reactivity Tertiary alcohol > Secondary alcohol > Primary alcohol	Order of reactivity CH_3OH > Primary alcohol > Secondary alcohol > Tertiary alcohol
Reactions <ol style="list-style-type: none"> $\text{C}_2\text{H}_5\text{OH} + \text{SOCl}_2 \xrightarrow{\text{Pyridine}} \text{C}_2\text{H}_5\text{Cl} + \text{SO}_2 + \text{HCl}$ Ethanol Thionyl chloride Ethyl chloride $\text{C}_2\text{H}_5\text{OH} + \text{HCl} \xrightarrow{\text{ZnCl}_2} \text{C}_2\text{H}_5\text{Cl} + \text{H}_2\text{O}$ 	Reactions <ol style="list-style-type: none"> $2\text{C}_2\text{H}_5\text{OH} + 2\text{Na} \longrightarrow 2\text{C}_2\text{H}_5\text{O}^-\text{Na}^+ + \text{H}_2$ Sodium ethoxide $\text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{COOH} \xrightleftharpoons{\text{H}_2\text{SO}_4} \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$ Ethyl acetate

Order of Stability of Carbocations is



Ter. carbocation Sec. carbocation Pri. carbocation Methyl carbocation

Order of Stability of Alkoxide ions is



Methoxide ion Pri. Alkoxide ion Sec. Alkoxide ion Ter. Alkoxide ion

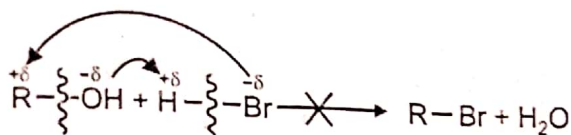
Reactions of Alcohols

(1) Reaction with HX to give Alkyl Halides

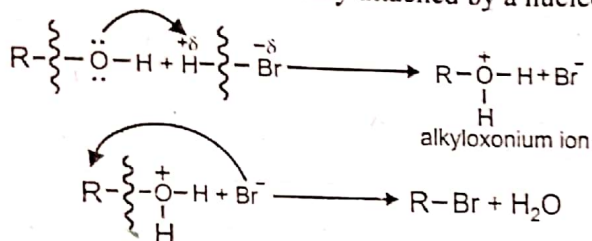
Due to the presence of unshared electron pairs on the oxygen atom of alcohols, they act as bases and react with halogen acids to form their respective alkyl halides.



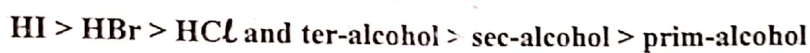
- The C-O bond in an alcohol is very slightly polarized. Therefore the following reaction mechanism is not possible.



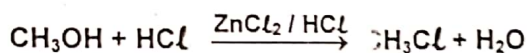
- In fact, the alcohol acting as a base first forms an alkyl oxonium ion. Now the C-O bond becomes highly polarized. This electrophile carbon is easily attacked by a nucleophile.



The orders of reactivity of halogen acids and alcohols are:



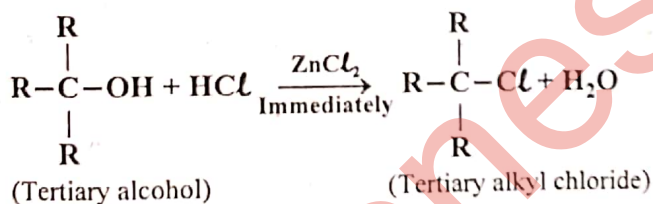
HCl and primary alcohols are the least reactive amongst halogen acids and alcohols respectively. Therefore they react only in the presence of a catalyst. A solution of ZnCl_2 in concentrated HCl is used as a catalyst.



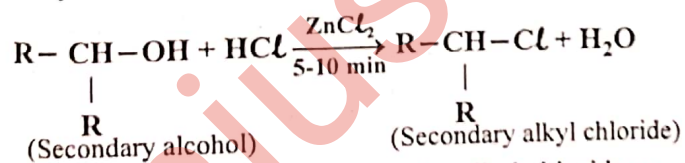
Lucas Test

The difference of chemical reactivity of alcohols with halogen is used for their identification. For this purpose alcohol is treated with a solution of ZnCl_2 in concentrated HCl.

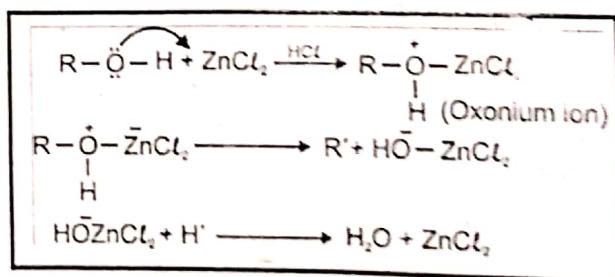
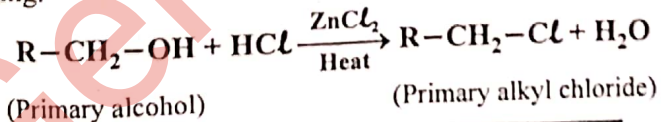
- (i) Tertiary alcohol immediately forms an insoluble layer of a ter-alkyl chloride.



- (ii) Secondary alcohol forms an insoluble sec-alkyl chloride in 5-10 minutes.



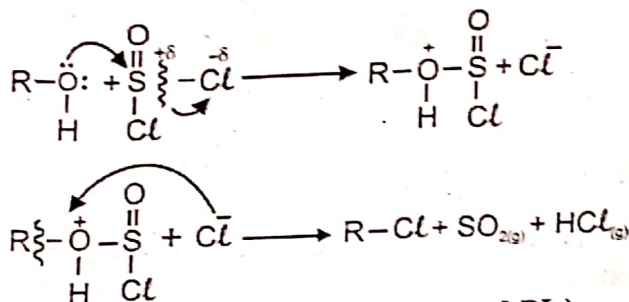
- (iii) Primary alcohol forms an insoluble prim-alkyl chloride on heating.



(2) Reaction with SOCl_2 , PX_3 to give Alkyl Halides

- (i) Thionyl chloride (SOCl_2)

Alcohols react with thionyl chloride to give alkyl chlorides.



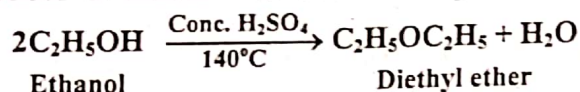
(ii) Phosphorus Tribromide and Triiodide (PBr₃ and PI₃)

Alkyl bromides and iodides are best prepared by treating alcohols with PBr₃ and PI₃.



(3) Acid catalyzed dehydration

Synthesis of Ethers via acid-catalyzed condensation of alcohols



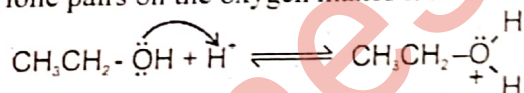
Elaboration

- Reagents typically H₂SO₄ and heat.
- In general, typically limited to symmetrical ethers of primary alcohols.
- The method is not suitable for unsymmetrical ethers.
- The substitution involves the 'O' nucleophile of one alcohol attacking the electrophilic 'C' in the other, displacing a water molecule.

Mechanism for alcohol condensation to give an ether

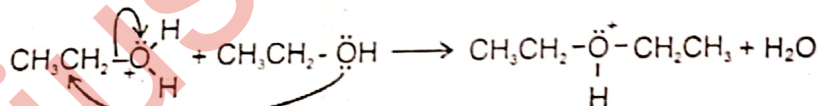
Step 1:

An acid/base reaction. Protonation of the alcoholic oxygen to make a better leaving group. This is very fast and reversible. The lone pairs on the oxygen makes it a Lewis base.



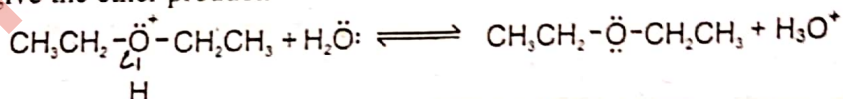
Step 2:

The 'O' of the second alcohol molecule functions as the nucleophile and attacks to displace the good leaving group, a neutral water molecule, by cleaving the C - O bond. This creates an oxonium ion intermediate.



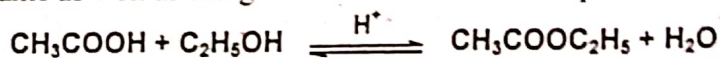
Step 3:

Another acid / base reaction. The proton is removed by a suitable base (here a water molecule, ROH is another alternative) to give the ether product.

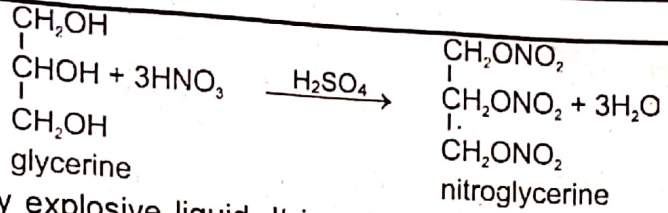


(4) Preparation of Esters (Esterification)

- Alcohols react with organic as well as inorganic acid to form their respective esters.

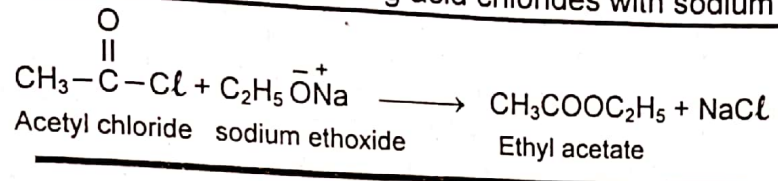


Glycerine reacts with a mixture of concentrated HNO₃ and H₂SO₄ to give an ester called Nitroglycerine or Glycerylnitrate.



Nitroglycerine is highly explosive liquid. It is mixed with fine sand and moulded into sticks called Dynamite.

- Esters are also formed by treating acid chlorides with sodium alkoxides.

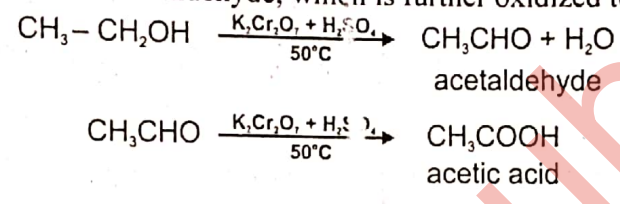


(5) Oxidation

Alcohols are easily oxidized by alkaline KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ solutions to give different products.

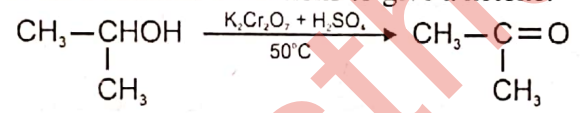
(i) Primary Alcohol:

A primary alcohol is first oxidized to an aldehyde, which is further oxidized to a carboxylic acid.



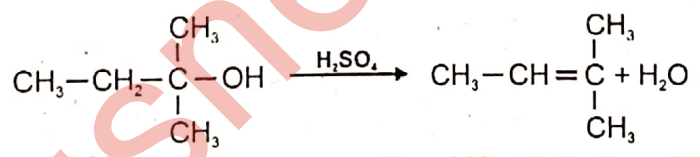
(ii) Secondary Alcohol:

A secondary alcohol is oxidized under similar conditions to give a ketone.

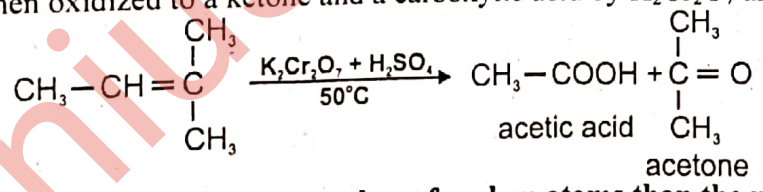


(iii) Tertiary Alcohol:

- A tertiary alcohol is not oxidized by alkaline KMnO_4 .
- When tertiary alcohol is heated with a mixture of $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 , it is first dehydrated to an alkene in the presence of acid.



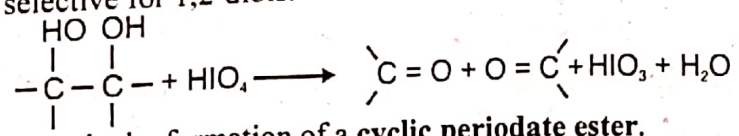
- The alkene is then oxidized to a ketone and a carboxylic acid by $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 .



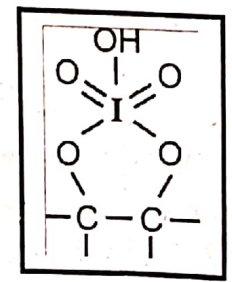
Each of the product contains lesser number of carbon atoms than the parent alcohol molecule.

Oxidative Cleavage of Diols

- 1,2- or vicinal diols are cleaved by periodic acid, HIO_4 , into two carbonyl compounds.
- The reaction is selective for 1,2-diols.



- The reaction occurs via the formation of a **cyclic periodate ester**.
- This can be used as a functional group test for 1,2-diols.
- The products are determined by the substituents on the diol.

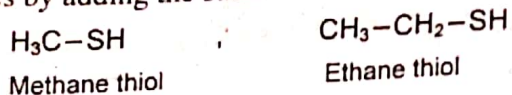


Cyclic periodate ester

The Sulfur Analogues (Thiols, RSH)

Nomenclature

Thiols are the sulfur analogues of alcohols. These are named by adding the suffix -Thiol to the name of corresponding alkanes. e.g.



Physical Properties

- In these compounds (thiols), hydrogen bonding is much weaker than that in alcohols.
- Thiols have lower boiling points than similar alcohols.

Structure

- Generally similar to alcohols, but bonds to 'S' are longer and weaker than those to 'O'.
- The thiol functional group consists of an 'S' atom bonded to a C atom and a H atom via σ -bonds.
- The S-H bond is less polar than that in alcohols (O-H) since 'S' is less electronegative than 'O'.

Reactivity

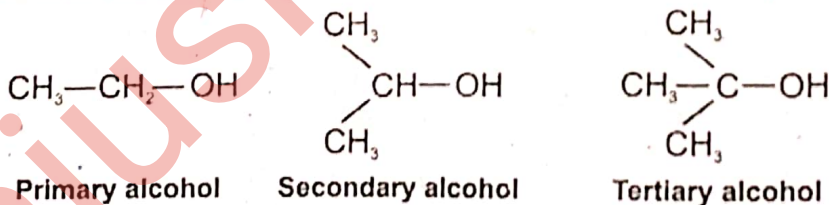
- Thiols are much more acidic than similar alcohols, e.g. RSH ($\text{pK}_a = 10$) versus ROH ($\text{pK}_a = 16$ to 19).
- Thiols are also much more nucleophilic than similar alcohols, in fact RSH is about as nucleophilic as RO^- .
- Thiols are readily oxidized due to S-O systems rather than C=S systems.
- Thiols are commonly oxidized to disulfides, R-S-S-R, a biologically important reaction.



1. What are monohydric and polyhydric alcohols?

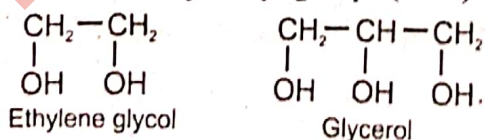
Ans. Monohydric Alcohols

- They contain one hydroxyl group (-OH).
- They are further classified into primary, secondary and tertiary alcohols.
- In primary alcohols, -OH functional group is attached with primary carbon atom, in secondary alcohols with secondary carbon atom and in tertiary alcohols it is attached with a tertiary carbon atom.



Polyhydric Alcohols

- They contain more than two hydroxyl groups (-OH).



12. Why some alcohols are readily soluble in water.

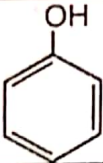
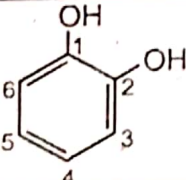
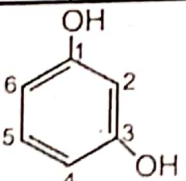
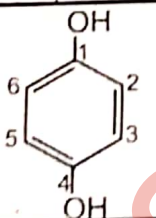
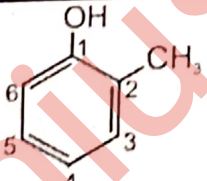
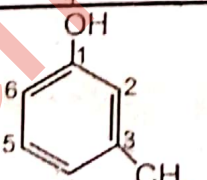
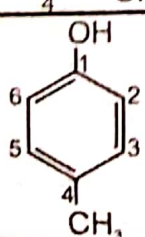
Ans. Lower alcohols are readily soluble in water but solubility decreases in higher alcohols. The solubility of alcohols due to hydrogen bonding which is more prominent in lower alcohols but less prominent in higher alcohols.

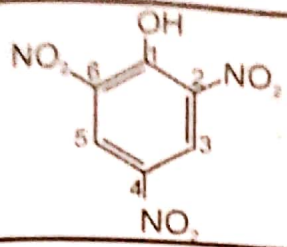
- The simplest example phenol is also known as carboic acid, i.e., C_6H_5OH .
- It was first obtained from coal tar by Runge in 1834.
- Phenol is derived from the old name for benzene (phene), to include the suffix that indicates it possesses a hydroxyl group (ol).
- Phenols can be obtained via **substitution** reactions, with the hydrolysis of diazonium salts being the most important laboratory method.
- Phenols are acidic and are important intermediates in the preparation of aryl ethers, C_6H_5-OR

Nomenclature

Phenols are named just like other derivatives of benzene. Anyhow, most of the members of this family have special names.

In IUPAC system, $-OH$ group is represented by name hydroxyl. It is used as a prefix, while the benzene part of the molecule is used as a suffix. Some common names, and their IUPAC names are given below:

Structure	IUPAC Name	Common Name
	Hydroxy phenol	Phenol (carboic acid)
	1,2-Dihydroxybenzene or o-hydroxy phenol	Catechol
	1,3-Dihydroxybenzene or m-hydroxy phenol	Resorcinol
	1,4-Dihydroxybenzene or p-hydroxy phenol	Hydroquinone
	2-Methylphenol	o-cresol
	3-Methylphenol	m-cresol
	4-Methylphenol	p-cresol

	2,4,6-Trinitrophenol	Picric acid
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Structure

- The alcohol functional group consists of an O atom bonded to an sp^2 -hybridized aromatic C atom and a H atom via σ bonds.
- Both the C–O and the O–H bonds are polar due to the high electronegativity of the O atom.
- Conjugation exists between an unshared electron pair on the oxygen and the aromatic ring.
- This results, as compared to simple alcohols is:
 - a shorter carbon-oxygen bond length.
 - a more basic hydroxyl oxygen
 - a more acidic hydroxyl proton ($\overset{\delta-}{O} - \overset{\delta+}{H}$)

Physical Properties

- Phenol is a colourless, crystalline, **deliquescent solid**.
- It has characteristic phenolic odour.
- It's melting point is 41°C and boiling point is 182°C .
- It is sparingly soluble in water forming pink solution at room temperature but completely soluble above 68.5°C .
- It is poisonous and used as a **disinfectant in hospitals and washrooms**.
- It causes blisters on the skin.
- It has distinctive odour.

Acidic strength $\propto 1/pK_a$

Acids	pKa
Sulphuric acid	-10.0
Hydrochloric acid	-9.0
Acetic acid	4.75
Phenol	10.0
Water	15.7
Ethanol	15.9

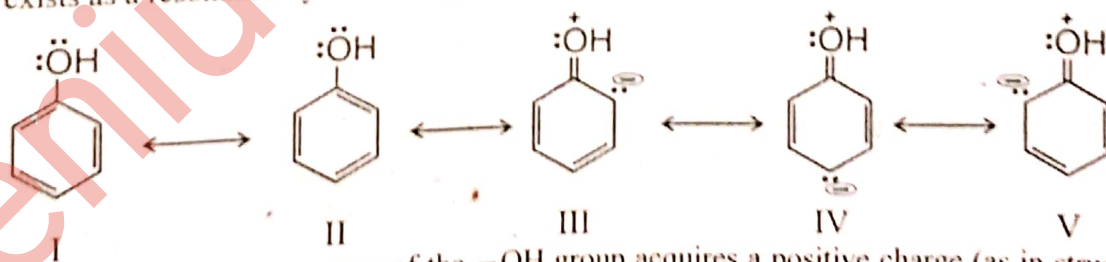
Acidic Behaviour of Phenol

- Phenols are more acidic ($pK_a \approx 10$) than alcohols ($pK_a \approx 16-20$), but less acidic than carboxylic acids ($pK_a \approx 5$).

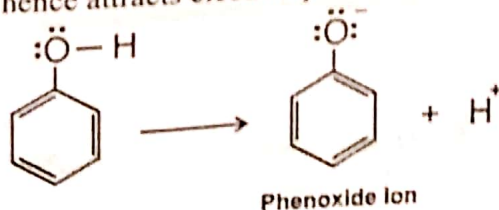
(i) Comparison of Acidity of Phenols and Alcohols

The stronger acidic nature of Phenols than alcohols can be explained as:

- (a) Phenol exists as a resonance hybrid of following structures:



Thus due to resonance oxygen atom of the –OH group acquires a positive charge (as in structures III to V) and hence attracts electron pair of O – H bond leading to the release of hydrogen atom as proton.

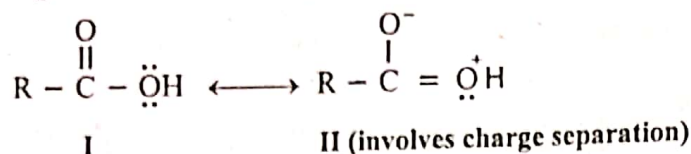


Carbon atom of the $> \text{COH}$ group in phenol being sp^2 -hybridized is more electron attracting than the sp^3 -hybridized carbon atom in alcohols. Thus in phenols there are greater I-effect which facilitates proton release. Thus phenols are more acidic than alcohols. Since resonance is impossible in alcohols (due to the absence of conjugation of the lone electron pair of oxygen with a double bond), the hydrogen atom is more firmly held to the oxygen atom. Hence alcohols are neutral in nature.

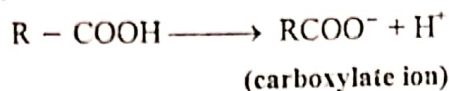
- (b) The negative Phenoxide ion formed after the release of hydrogen atom is more resonance stabilized than phenol. Since there is no possibility for the delocalization of negative charge in the alkoxide ion, the latter is not stable. Hence alcohols have no tendency to form alkoxide and hydrogen ion.

(ii) Comparison of Acidity of Phenols and carboxylic acid

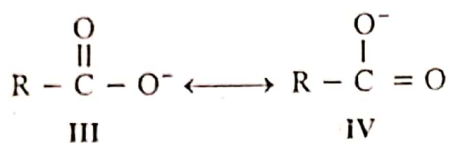
Resonating structures of carboxylic acids are:



Carboxylic acids ionize as:

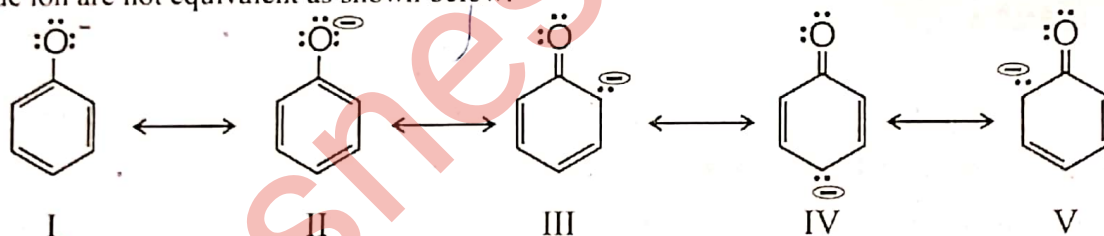


The carboxylate anion so formed exhibits the following resonating structures:



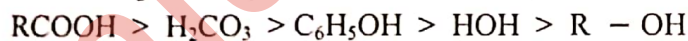
Now the resonating structures I and II of carboxylic acid are non-equivalent and hence much less stable than the equivalent resonating structures III and IV for the carboxylate ion. Thus carboxylic acids have a tendency to undergo ionization to form more stable carboxylate ion and protons.

Now let us compare the acidic strengths of carboxylic acids and phenols. The resonating structures of phenoxide ion are not equivalent as shown below:



The resonating structures III and IV of carboxylate anions are equivalent. Hence carboxylate anion is relatively more resonance stabilized than the phenoxide ion. Thus a carboxylic acid is more acidic than a phenol.

(iii) Relative acidity of some common compounds follows the order:



(iv) Effect of substituents on the acidity of Phenols

Electron attracting substituents tend to disperse the negative charge of the phenoxide ion, thus stabilize the ion and increase the acidity of phenols. Electron releasing substituents tend to intensify the charge, destabilize the ion, diminish the resonance and decrease its acidity.

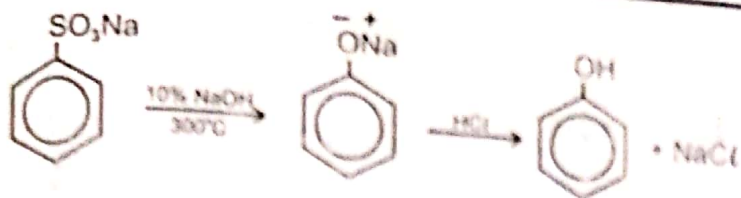
Exercise: Q.3(6) Give at least two methods for the preparation of phenol.

Preparations of Phenols

Industrial (Large scale) preparation of Phenol

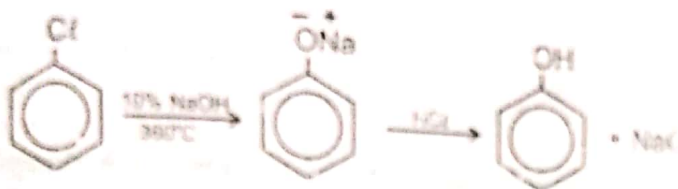
(i) Reaction of Sodium salt of Benzene Sulfonic Acid with Sodium Hydroxide

Sodium benzene sulphonate on fusion with strong alkali like NaOH at 300°C give sodium phenoxide which on treatment with HCl gives phenol.



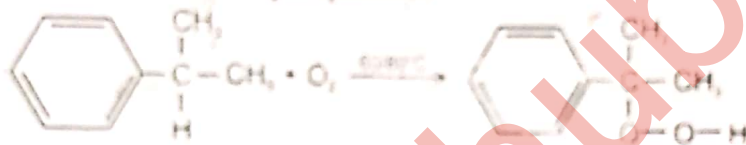
(ii) Base Hydrolysis of Chlorobenzene (Dow's Method)

Chlorobenzene is hydrolyzed by heating with 10% NaOH at 360°C and under high pressure to form sodium phenoxide which on treating with HCl gives phenol.

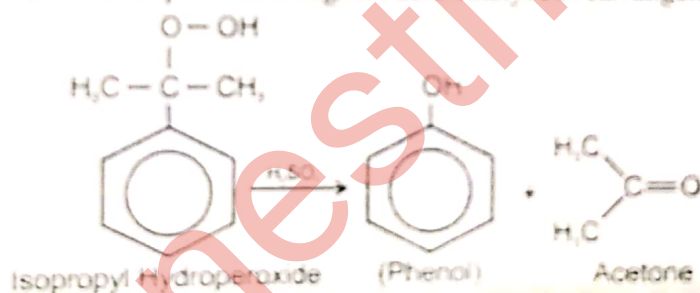


(iii) Acidic oxidation of cumene

It is recently developed commercial method for the preparation of phenol. Cumene is oxidized by atmospheric oxygen in presence of metal catalyst, into cumene hydroperoxide.



The hydroperoxide is converted into phenol through an acid catalyzed rearrangement.

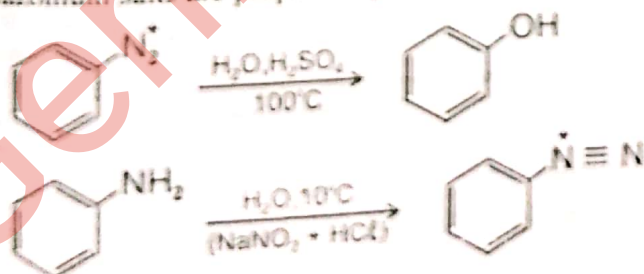


Laboratory Preparation

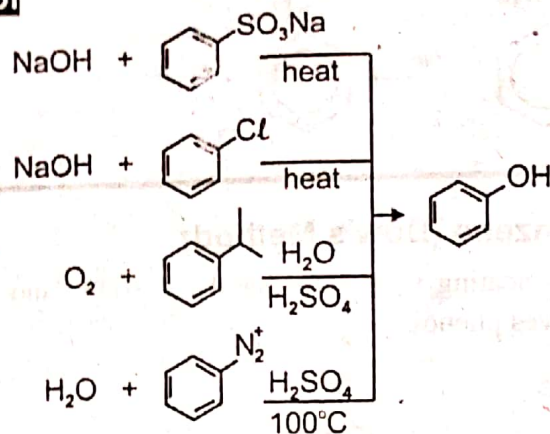
Preparation of Phenols from Aryl Diazonium Salts

Elaboration

- Aryl diazonium salts can be converted into phenols using $H_2O / H_2SO_4 / \text{heat}$
- Aryl diazonium salts are prepared by reaction of aryl amines with nitrous acid, HNO_2 .



Preparation summary of phenol



Reactivity

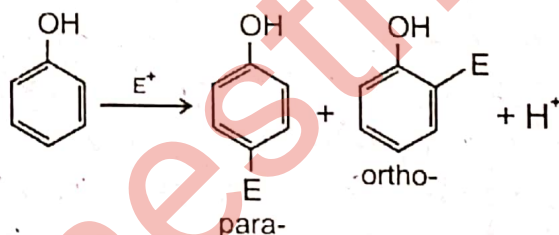
Phenols are very reactive towards electrophilic aromatic substitution. This is because the hydroxyl group, $-\text{OH}$, is a strongly activating, ortho- / para- directing substituent.

Reactions of Phenols

(i) Electrophilic Aromatic Substitution

Elaboration

- Phenols are potentially very reactive towards electrophilic aromatic substitution. This is because the hydroxyl group, $-\text{OH}$, is a strongly activating, ortho and para- directing substituent.
- Substitution typically occurs para to the hydroxyl group unless the para position is blocked; then ortho substitution occurs.
- The strong activation often means that milder reaction conditions than those used for benzene itself can be used. Phenols are so activated that polysubstitution can be a problem.

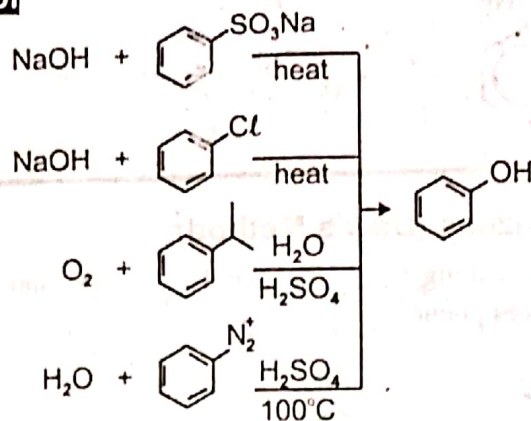


Reaction	Phenol	Benzene
Nitration	dil. HNO_3 in H_2O or $\text{CH}_3\text{CO}_2\text{H}$	$\text{HNO}_3 / \text{H}_2\text{SO}_4$
Sulphonation	conc. H_2SO_4	H_2SO_4 or $\text{SO}_3 / \text{H}_2\text{SO}_4$
Halogenation	X_2	X_2 / Fe or FeX_3
Alkylation	ROH / H^+ or $\text{RCl} / \text{AlCl}_3$	$\text{RCl} / \text{AlCl}_3$
Acylation	$\text{RCOCl} / \text{AlCl}_3$	$\text{RCOCl} / \text{AlCl}_3$
Nitrosation	aq. $\text{NaNO}_2 / \text{H}^+$	

(ii) Reaction with Sodium Metal

Carboxylation of Phenols (Kolbe-Schmitt reaction)

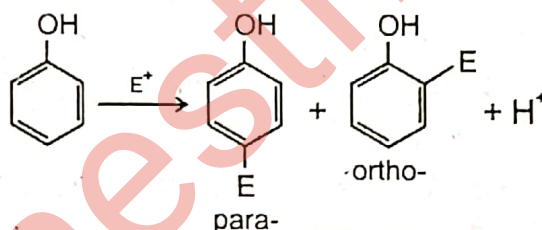
- The reaction of sodium salt of phenol with CO_2 is called Kolbe reaction. It is carbonation of phenol.
- At low temperature sodium salicylate (sodium-o-hydroxy benzoate), whereas at higher temperature o-product isomerizes to p-isomer.
- Carbon of CO_2 acts as electrophilic centre in this reaction.
- Acidification of the salt gives corresponding hydroxyl acid.

Preparation summary of phenol**Reactivity**

Phenols are very reactive towards electrophilic aromatic substitution. This is because the hydroxyl group, $-\text{OH}$, is a strongly activating, ortho- / para- directing substituent.

Reactions of Phenols**(i) Electrophilic Aromatic Substitution****Elaboration**

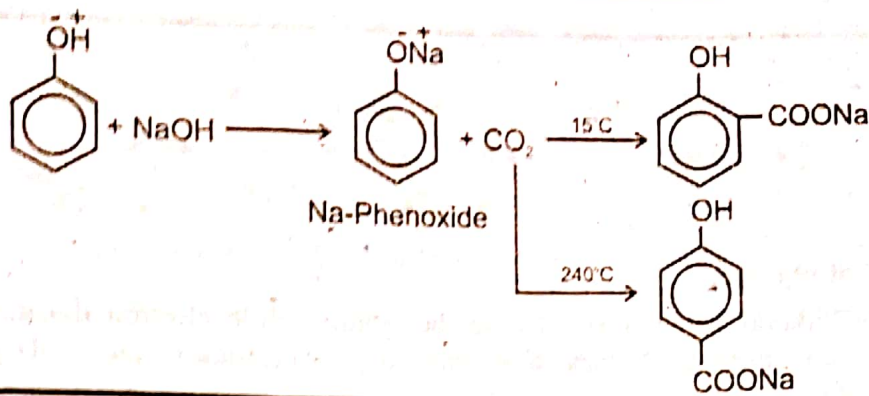
- Phenols are potentially very reactive towards electrophilic aromatic substitution. This is because the hydroxy group, $-\text{OH}$, is a strongly activating, ortho and para- directing substituent.
- Substitution typically occurs para to the hydroxyl group unless the para position is blocked; then ortho substitution occurs.
- The strong activation often means that milder reaction conditions than those used for benzene itself can be used. Phenols are so activated that polysubstitution can be a problem.



Reaction	Phenol	Benzene
Nitration	dil. HNO_3 in H_2O or $\text{CH}_3\text{CO}_2\text{H}$	$\text{HNO}_3 / \text{H}_2\text{SO}_4$
Sulphonation	conc. H_2SO_4	H_2SO_4 or $\text{SO}_3 / \text{H}_2\text{SO}_4$
Halogenation	X_2	X_2 / Fe or FeX_3
Alkylation	ROH / H^+ or $\text{RCl} / \text{AlCl}_3$	$\text{RCl} / \text{AlCl}_3$
Acylation	$\text{RCOCl} / \text{AlCl}_3$	$\text{RCOCl} / \text{AlCl}_3$
Nitrosation	aq. $\text{NaNO}_2 / \text{H}^+$	

(ii) Reaction with Sodium Metal**Carboxylation of Phenols (Kolbe-Schmitt reaction)**

- The reaction of sodium salt of phenol with CO_2 is called Kolbe reaction. It is carbonation of phenol.
- At low temperature sodium salicylate (sodium-o-hydroxy benzoate), whereas at higher temperature o-product isomerizes to p-isomer.
- Carbon of CO_2 acts as electrophilic centre in this reaction.
- Acidification of the salt gives corresponding hydroxyl acid.



(iii) Oxidation of Phenols

Phenols are very reactive towards oxidizing agents. The oxidation takes place through several steps eventually destroying the ring.

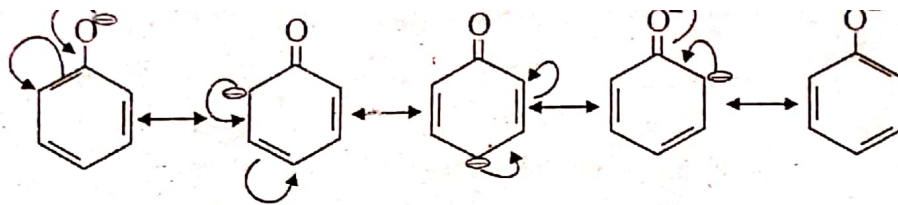
Difference between Alcohols and Phenol

The main difference between alcohols and phenols are as follow:

Alcohols	Phenols
• In alcohols, hydroxyl group is attached to an alkyl group.	• In phenols, hydroxyl group is attached to an aryl group.
• Alcohols are hydroxy derivatives of alkanes.	• Phenols are hydroxy derivatives of benzene.
• In alcohols, one hydrogen of water is replaced by an alkyl group.	• In phenols, one hydrogen of water is replaced by an aryl group.
• The general formula of alcohols is R-OH.	• The general formula of phenol is C ₆ H ₅ OH. It is also known as carbolic acid.
• Alcohols may be monohydric and polyhydric depending on the number of -OH groups attached.	• Phenols are not monohydric or polyhydric.
• Lower alcohols are generally colorless liquids.	• They are colorless, crystalline, deliquescent solids.
• Alcohols have a characteristic sweet smell and burning taste.	• They have characteristic phenolic odor. Melting point of carbolic acid (phenol) is 41°C.
• They are readily soluble in water but solubility decreases in higher alcohols.	• Carbolic acid is sparingly soluble in water forming pink solution at room temperature but completely soluble above 68.5°C.
• Alcohol reacts with other reagents in two ways, either in which C-O bond breaks or in which O-H bond breaks.	• Phenolate ions have resonance structures but alcohols don not have such type structures.
• Alcohols are less acidic (pKa ≈ 16-20) than phenols (pKa ≈ 10).	• Phenols are more acidic (pKa ≈ 10) than alcohols (pKa ≈ 16-20).

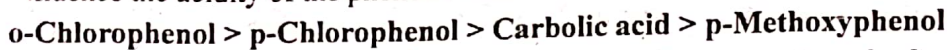
QUICK QUIZ

1. How negative charge of phenolate ion is stable?
 Ans. In phenolate ion, the negative charge on oxygen atom can become involved with the π- electron cloud on the benzene ring. The negative charge is thus delocalized in the ring and the phenoxide ion becomes relatively stable.



2. What is acidity order of phenols?

Ans. In phenols, electron withdrawing groups increase the acidity while electron donating groups decrease the acidity. Substituents, particularly those located at ortho or para position to the $-OH$ group, can dramatically influence the acidity of the phenols.



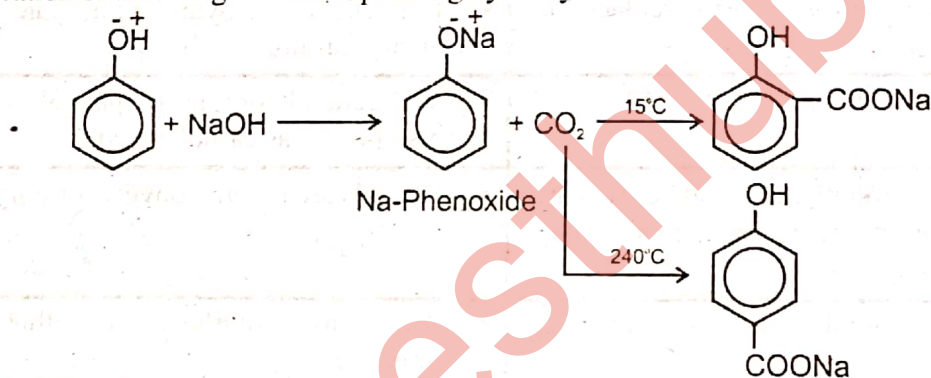
3. Why phenols are very reactive towards electrophilic aromatic substitution?

Ans. Phenols are potentially very reactive towards electrophilic aromatic substitution. This is because the hydroxy group, $-OH$, is a strongly activating, ortho and para- directing substituent.

4. Explain carbonation of phenols.

Ans. Carboxylation of Phenols (Kolbe-Schmitt reaction)

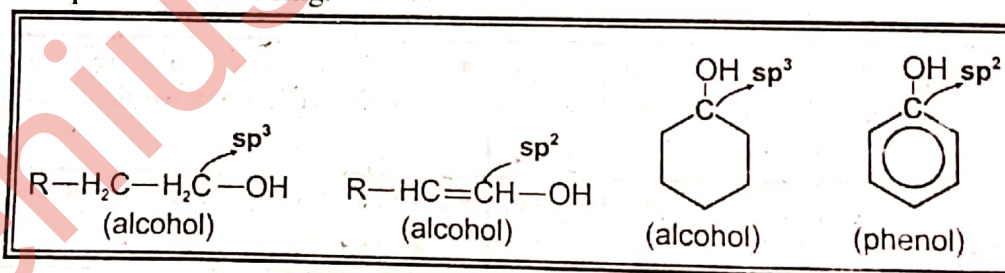
- The reaction of sodium salt of phenol with CO_2 is called Kolbe reaction. It is carbonation of phenol.
- At low temperature sodium salicylate (sodium- o -hydroxy benzoate), whereas at higher temperature o -product isomerizes to p -isomer.
- Carbon of CO_2 acts as electrophilic centre in this reaction.
- Acidification of the salt gives corresponding hydroxyl acid.



5. Alcohols and phenols both contain $-OH$ group. What is difference between them

Ans. Alcohols are the hydroxy derivatives of hydrocarbons. In alcohols the OH group is attached to sp^3 hybridized carbon or sp^2 hybridized carbon which is not the part of benzene ring.

Phenols are the hydroxy derivatives of benzene. In phenols the OH group is attached to sp^2 hybridized carbon which is the part of benzene ring.

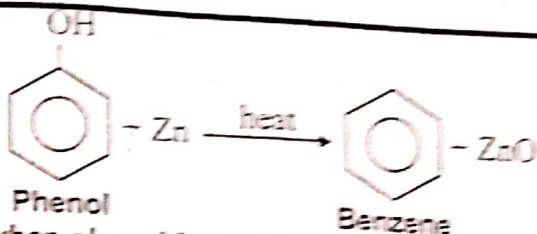


6. Why phenol is more acidic than ethyl alcohol?

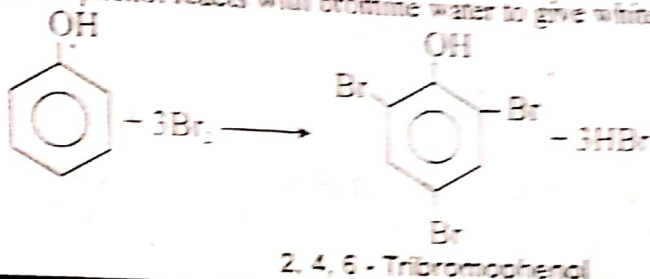
Ans. When phenol is dissolved in water, it ionizes to phenoxide ion. In phenoxide ion, the negative charge on oxygen atom can become involved with the π - electron cloud on the benzene ring. The negative charge is thus delocalized in the ring and the phenoxide ion becomes relatively stable. This type of delocalization is not possible with ethoxide ion of ethyl alcohol. This makes phenol more acidic than ethyl alcohol.

7. What happens when phenol is heated with zinc dust?

Ans. When phenol is heated with zinc dust, benzene is formed.



5. What happens when phenol is treated with bromine water?
 Ans. An aqueous solution of phenol reacts with bromine water to give white ppt. of 2, 4, 6-Tribromophenol.

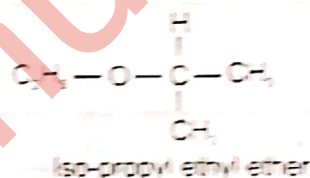
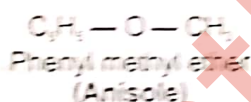
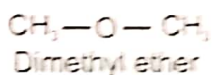


ETHERS

Nomenclature

(i) Common System of Naming

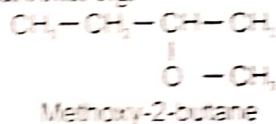
In common system of naming, simple and mixed (or unsymmetrical) ethers are named by naming the two groups bonded to oxygen followed by the word 'ether', e.g.



(ii) IUPAC System

In IUPAC system the large alkyl (R) group is taken as parent molecule and given the last name (suffix) while the smaller alkyl group along with oxygen is used as prefix and given the name alkoxy (e.g. methoxy, ethoxy, propoxy, etc.). IUPAC names are not common as they are difficult.

Mixed ether are named as alkyl derivatives of hydrocarbons, e.g.



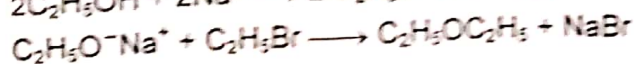
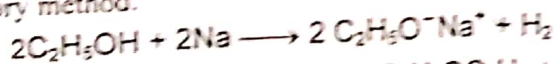
Formula	Common Names	IUPAC
CH_3OCH_3	Dimethyl ether	Methoxy methane
$\text{CH}_3\text{OC}_2\text{H}_5$	Methyl ethylether	Methoxy ethane
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	Diethyl ether	Ethoxy ethane
$\text{C}_2\text{H}_5\text{OCH}_2 - \text{CH}_2 - \text{CH}_3$	Ethyl n-propylether	Ethoxy n - propane
$\text{CH}_3\text{OC}_6\text{H}_5$	Methyl phenylether (Anisole)	Methoxy benzene

Preparation

Ethers are prepared by the following methods:

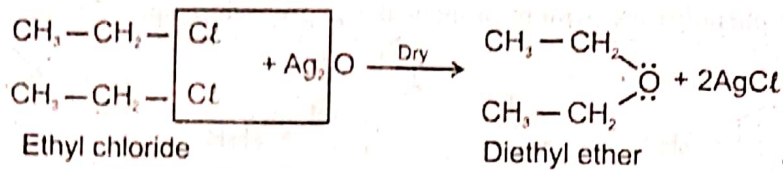
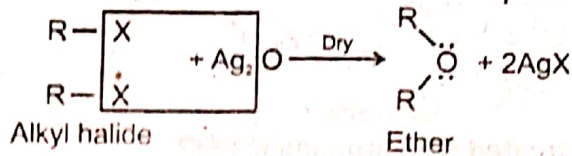
(a) Williamson synthesis:

When alkyl halides are heated with sodium or potassium alkoxide, then ethers are produced. This is one of the most important laboratory method.



(II) Reaction of alkyl halides with dry Ag₂O

When alkyl halides are heated with dry silver oxide, then ethers are produced

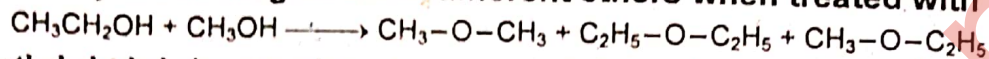


MCQ's

The product formed when an alkyl halide is treated with moist Ag₂O

- (a) Alcohol
- (b) Carboxylic acid
- (c) Ether
- (d) Alkane

(III) Two different primary alcohols give three different ethers when treated with H₂SO₄.



Ter-butyl and ethyl alcohol give one ether.

Physical Properties

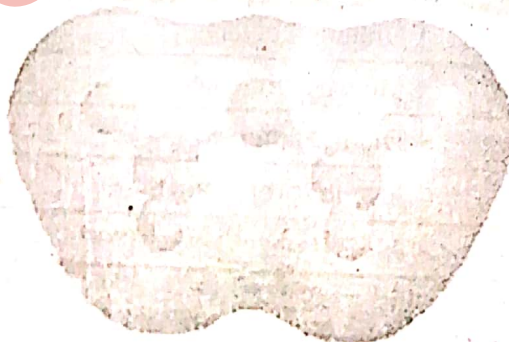
- Ethers are colorless, low boiling and highly inflammable compounds.
- Their chemical inactivity and their ability to dissolve fats, oil, gum and many other organic compound make them very good solvent.
- Ethers are soluble in concentrated sulphuric acid, a characteristic of oxygen containing compounds. This property is used as a test to distinguish between ethers and saturate hydrocarbons.
- Lower ethers act as anaesthetics.
- Ethers are lighter than water.

Exercise: Q.3(5) Give the reactivity of ethers.

Chemical Reactivity

The image shows the electrostatic potential for dimethyl ether. The more **dark** an area has high electron density and the more **light** area has low electron density.

- The ethereal 'O' atom is a region of high electron density (**dark**) due to the lone pairs.
- Ethers are Lewis bases.
- Like an alcohol -OH group, the -OR group is a poor leaving group and needs to be converted to a better leaving group before substitution can occur.
- The most important reactions of ethers is their cleavage by strong acids such as HI or HBr.



1. How ethers show resistance to oxidation?

Ans. Resistance to Oxidation:

Ethers are resistant to attack by the usual chemical oxidizing agents. Moreover, reagent like NH₃, Na, alkalis and acids have no action on ethers.



Organometallic compounds in medicines

1. Antiseptics and Disinfectants

Antiseptics and disinfectants are an essential part of infection control practices and aid in the prevention of nosocomial infections. They are extensively used in hospitals and other health care settings for a variety of topical and hard surface applications. A wide variety of active chemical agents or biocides are found in these products many of which have been used for hundred of years for antiseptics, disinfection and preservation. In general, biocides have a broader spectrum of activity than antibiotics. The widespread use of antiseptic and disinfectant products has promoted some speculation on the development of microbial resistance, in particular cross-resistance to antibiotics. Anti microbial activity of antiseptics and disinfectants can be influenced by many factors e.g. formulation effects, presence of an organic load, temperature, dilution etc.

Antiseptics

An antiseptic is a substance which inhibits the growth and development of micro organisms. For practical purposes, antiseptics are thought of as topical agents for application to skin, mucous membrane and inanimate objects. They can be either bactericidal or bacteriostatic. Their uses include cleansing of skin and wound, surfaces after injury, preparation of skin surface prior to injection or surgical procedure and routine disinfection of oral cavity as part of oral hygiene.

Disinfectants

Disinfectants were introduced by Lister who introduced carbolic acid (phenol) as the first disinfectant. Today disinfectants are widely used in the health care, food and pharmaceutical sectors to prevent unwanted micro-organisms from causing disease. Disinfectants chemicals disrupt significant cellular structures or processes in order to kill and eliminate micro-organisms.

2. Ether – An effective Anaesthetic

Before the advent of anaesthetics, surgery was a savage and primitive affair. It was agony for the patient, and surgeons were therefore only prepared to operate if it was absolutely essential, for example, the amputation of a damaged limb that would otherwise become gangrenous. Anaesthetics enable surgery to develop from crude carpentry to its present sophisticated forms.

Three of the most important early anaesthetics were nitrous oxide (dinitrogen oxide, N_2O), ether (ethoxyethane, $CH_3CH_2OCH_2CH_3$) and chloroform (trichloromethane, $CHCl_3$).

- Nitrous oxide (N_2O) is non-toxic and non-flammable, but it only produces light anaesthesia.
- Chloroform ($CHCl_3$) produces deep anaesthesia and is non-flammable, but it is toxic and carries the risk of liver damage.

KEY POINTS

- Alcohols and phenols are hydroxyl derivatives of aliphatic and aromatic hydrocarbons.
- General formula for alcohol is ROH, for Phenol PhOH, and for ether it is ROR.
- Alcohols are usually named by replacing 'e' from the Alkane with 'ol'.
- Primary alcohols can be oxidized.
- Secondary alcohols can be oxidized to ketones but no further.
- Tertiary alcohols cannot be oxidized (no carbinol C-H).
- The thiol functional group consists of an S atom bonded to a C atom and a H atom via σ -bonds.
- Thiols are much more acidic than similar alcohols, e.g. RSH ($pK_a = 10$) versus ROH ($pK_a = 16$ to 19)
- Phenols are more acidic ($pK_a \approx 10$) than alcohols ($pK_a \approx 16-20$), but less acidic than carboxylic acids ($pK_a \approx 5$)

- Epoxides are more reactive than simple ethers.
- In IUPAC system, ethers are named as alkoxy derivatives of alkanes.
- In contrast to alcohol, ethers are fairly unreactive.
- Alcohols are soluble in water while phenols are sparingly soluble.
- General formula for alcohol is $R-OH$ while for phenol is $Ar-OH$.
- Methyl alcohol has proved to be excellent fuel for racing car.
- Ethyl alcohol may be the first organic chemical routinely manufactured by humans.
- Ethyl alcohol is also named as wine, beer and whiskey.
- Fuel oil mainly consists of amyl alcohol ($C_5H_{11}OH$)
- 95% ethyl alcohol is known as rectified spirit or commercial alcohol.
- Ethylene glycol is the major component in commercial coolants and anti-freeze.
- Glycerol is an excellent moisture retaining agent. It is used in vanishing creams, body lotions, shaving foams and tooth pastes.
- Bakelite (plastic) is a polymer formed from phenol and formaldehyde.
- Phenol is used as starting material for drugs such as salol, aspirin, phenolphthalein and several other dyes.
- Diethyl ether has been used in surgery for anaesthesia.
- Cyclic ethers are known as epoxides.

EXERCISE

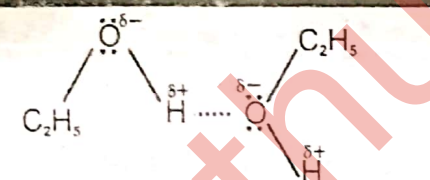
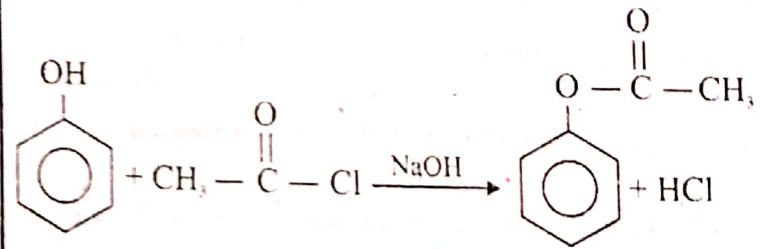
Q1. Multiple Choice Questions. Encircle the correct answer:

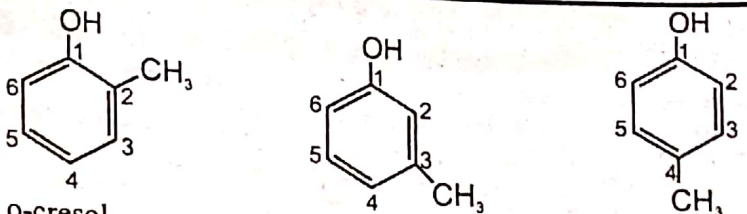
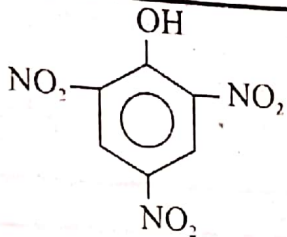
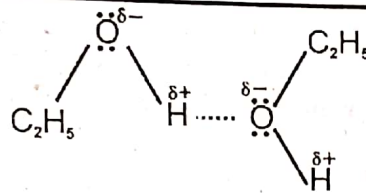
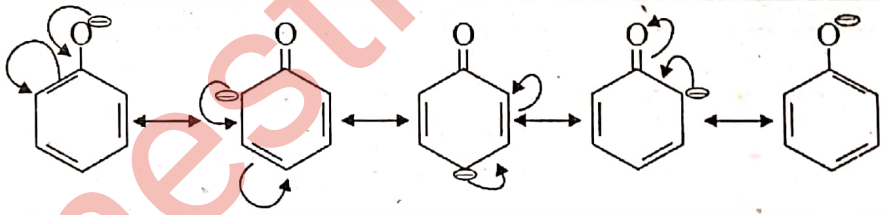
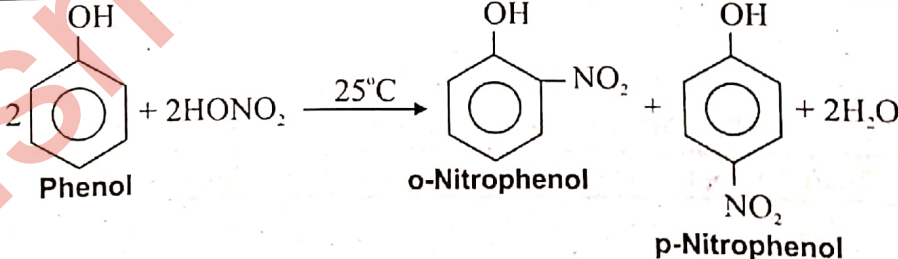
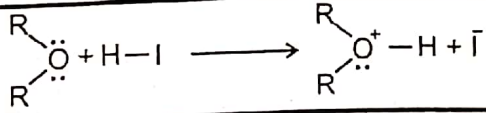
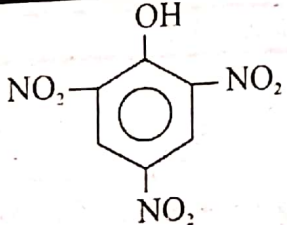
- ★ Read the question carefully.
- ★ Try to answer the question yourself before reading the answer choices.
- ★ Guess only if you can eliminate one or more answer choices.
- ★ Drawing a picture can help.
- ★ Don't spend too much time on any one question.
- ★ In-depth calculations are not necessary; approximate the answer by rounding.

- (i) Which compound shows hydrogen bonding?
 (a) C_2H_6 (b) C_2H_5Cl (c) CH_3-O-CH_3 (d) C_2H_5OH
- (ii) Which compound is called a universal solvent?
 (a) H_2O (b) CH_3OH (c) C_2H_5OH (d) CH_3-O-CH_3
- (iii) According to Lewis concept ethers behave as
 (a) acid (b) base (c) acid as well as base (d) none of them
- (iv) Ethanol can be converted into ethanoic acid by
 (a) hydrogenation (b) hydration (c) oxidation (d) fermentation
- (v) Ethanol is denatured by adding;
 (a) methanol (b) carbolic acid (c) acetone (d) propanol
- (vi) When phenol reacts with CH_3COCl the product formed is;
 (a) ether (b) alcohol (c) aldehyde (d) ester
- (vii) Williamsons synthesis of ethers is superior to alcohols because it makes
 (a) symmetrical ethers (b) asymmetrical ethers
 (c) ether at room temperature (d) both symmetrical and asymmetrical Ethers.
- (viii) A methyl phenol is also called
 (a) cresol (b) benzyl alcohol (c) alcohol (d) formaldehyde

- (ix) Which one of the following compounds does not contain carboxylic group?
 (a) acetic acid (b) formic acid (c) benzoic acid (d) picric acid
- (x) Hydrogen bonding is maximum in
 (a) diethyl ether (b) ethanal (c) ethyl alcohol (d) triethyl amine
- (xi) Which of the following compounds have no attraction at all with water?
 (a) C_6H_6 (b) C_2H_5OH (c) $CH_3CH_2CH_2OH$ (d) $CH_3-O^-CH_3$
- (xii) Phenols are more acidic than alcohols which statement is correct?
 (a) phenol turns blue litmus paper red (b) alcohol liberates CO_2 with carbonate solution
 (c) phenoxide ion is stabilized due to resonance (d) alkoxide ion is stabilized due to resonance
- (xiii) Carboic acid is treated with dilute nitric acid at $25^\circ C$, the product is
 (a) o-nitrophenol (b) p-nitrophenol (c) m-nitrophenol (d) both a and b
- (xiv) Oxonium ion is formed when
 (a) ethanol reacts with Na metal (b) phenol reacts with NaOH solution
 (c) ether is treated with HI (d) ethanol is treated with aq. NaOH and iodine
- (xv) 2,4,6-Trinitrophenol is commercially called as
 (a) TNT (b) picric acid (c) carboic acid (d) fumeric acid

SOLVED EXERCISE MCQs

Q. No	Answer	Reason
(i)	(d) C_2H_5OH	 <p>Hydrogen bonding in ethanol</p>
(ii)	(a) H_2O	Water dissolves almost all compounds except some organic compounds so it is a universal solvent.
(iii)	(b) base	Ether can give lone pair of electrons so they are Lewis base.
(iv)	(c) oxidation	$C_2H_5OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3CHO \xrightarrow{[O]} CH_3COOH$ <p>(Ethanol) (Ethanoic acid)</p>
(v)	(a) methanol	Ethanol is denatured by addition of 10% methanol to avoid its use for drinking purposes. Such alcohol is called methylated spirit. A small quantity of pyridine or acetone may also be added for this purpose.
(vi)	(d) ester	Phenol reacts with acetyl chloride in the presence of a base to form ester.  <p>Phenyl acetate</p>
(vii)	(d) both symmetrical and asymmetrical Ethers	When alkyl halides are heated with sodium or potassium alkoxide, then ethers are produced. This is the most important laboratory method. $2C_2H_5OH + 2Na \longrightarrow 2C_2H_5O^-Na^+ + H_2$ $C_2H_5O^-Na^+ + C_2H_5Br \longrightarrow C_2H_5OC_2H_5 + NaBr$

(viii)	(a) cresol	 <p>o-cresol m-cresol p-cresol</p>
(ix)	(d) picric acid	 <p>2,4,6-Trinitrophenol (Picric acid)</p>
(x)	(c) ethyl alcohol	 <p>Hydrogen bonding in ethanol</p>
(xi)	(a) C ₆ H ₆	Benzene is non-polar while H ₂ O is polar so C ₆ H ₆ (benzene) is insoluble in water.
(xii)	(c) phenoxide ion is stabilized due to resonance	
(xiii)	(d) both a and b	 <p>Phenol o-Nitrophenol p-Nitrophenol</p>
(xiv)	(c) ether is treated with HI	
(xv)	(b) picric acid	 <p>2,4,6-Trinitrophenol (Picric acid)</p>

SHORT ANSWERS QUESTIONS

2. Give brief answers for the following questions.

(i) What are alcohols? How are they classified?

Ans. Alcohols:

The organic compounds containing hydroxyl group $-OH$, as functional group are called alcohols.

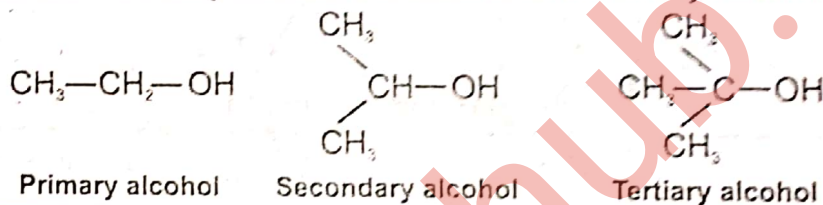
Classification of alcohols:

Alcohols containing one $-OH$ group are called monohydric alcohols and those containing two or more hydroxyl groups are known as polyhydric alcohol.

(ii) How are monohydric alcohols classified?

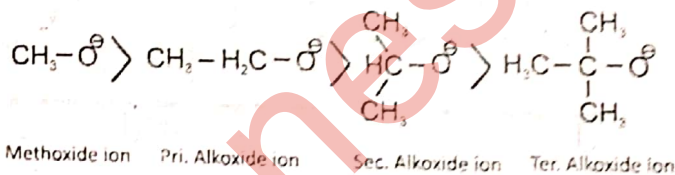
Ans. Monohydric Alcohols

- They contain one hydroxyl group ($-OH$).
- They are further classified into primary, secondary and tertiary alcohols.
- In **primary alcohols**, $-OH$ functional group is attached with primary carbon atom, in **secondary alcohols** with secondary carbon atom and in **tertiary alcohols** it is attached with a tertiary carbon atom.



(iii) Compare the acidity of primary, secondary and tertiary alcohols.

Ans. When an alcohol is dissolved in water, it loses proton (H^+) and alkoxide ion is formed. The acidity of alcohol depends upon the stability of alkoxide ion which is:

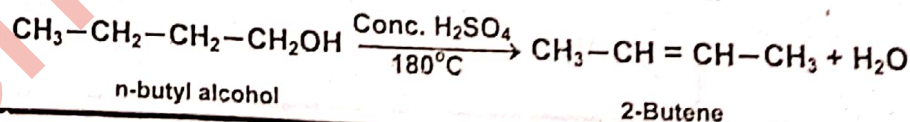


Therefore, the order of acidity of alcohols is:

Primary alcohol > secondary alcohol > tertiary alcohol

(iv) 2-Butene is the major product when n-butyl alcohol is heated with conc. H_2SO_4 . Explain.

Ans. Conc. H_2SO_4 is a strong dehydrating agent. When it is heated with n-butyl alcohol, dehydration takes place and 2-Butene is produced. During this reaction $C-O$ and $C-H$ bond break.

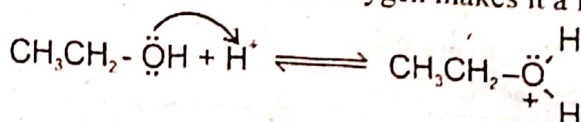


(v) Give the mechanism of dehydration of alcohols.

Ans. Mechanism of dehydration of alcohols

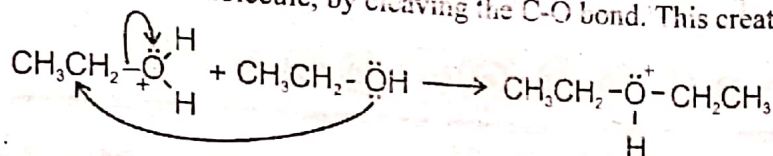
Step 1:

An acid/base reaction. Protonation of the alcoholic oxygen to make a better leaving group. This is fast and reversible. The lone pairs on the oxygen makes it a Lewis base.



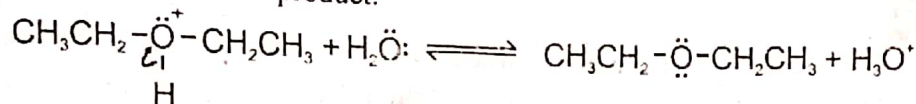
Step 2:

The 'O' of the second alcohol molecule functions as the nucleophile and attacks to displace the good leaving group, a neutral water molecule, by cleaving the C-O bond. This creates an oxonium ion intermediate.



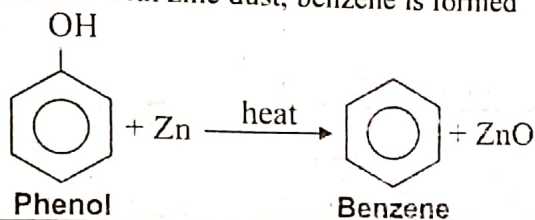
Step 3:

Another acid / base reaction. The proton is removed by a suitable base (here a water molecule, ROH is another alternative) to give the ether product.



(vi) How will you obtain benzene from phenol?

Ans. When phenol is heated with zinc dust, benzene is formed

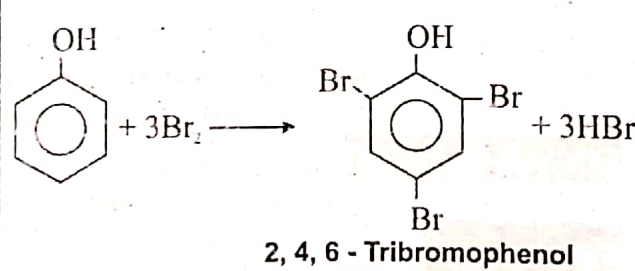


(vii) Alcohols and phenols both have OH group but phenols are more acidic than alcohols.

Ans. When phenols are dissolved in water, they ionize to phenoxide ions. In phenoxide ion, the negative charge on oxygen atom can become involved with the π -electron cloud on the benzene ring. The negative charge is thus delocalized in the ring and the phenoxide ion becomes relatively stable. This type of delocalization is not possible with alkoxide ions of alcohols. This makes phenols more acidic than alcohols.

(viii) How will you differentiate between alcohol and phenol?

Ans.

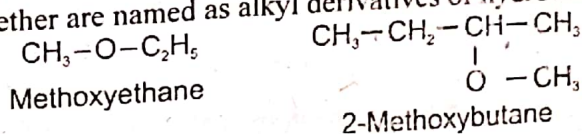
Alcohol	Phenol
It gives positive iodoform test i.e. on treating with conc. HCl in the presence of anhydrous ZnCl_2 , an alcohol forms oily layer.	An aqueous solution of phenol reacts with bromine water to give white ppt. of 2, 4, 6-Tribromophenol.
$\text{R}-\text{CH}_2-\text{OH} + \text{HCl} \xrightarrow[\text{heat}]{\text{ZnCl}_2} \text{R}-\text{CH}_2-\text{Cl} + \text{H}_2\text{O}$	
	2, 4, 6 - Tribromophenol

(ix) Write the nomenclature of ether by IUPAC system.

Ans. Nomenclature of ether by IUPAC system:

In IUPAC system the large alkyl (R) group is taken as parent molecule and given the last name (suffix) while the smaller alkyl group along with oxygen is used as prefix and given the name alkoxy (e.g. methoxy, ethoxy, propoxy, etc). IUPAC names are not common as they are difficult.

Mixed ether are named as alkyl derivatives of hydrocarbons, e.g.



(x) Why is phenol more soluble in water than toluene?

Ans. Due to presence of $-OH$ group in phenol it is more soluble in water than toluene which has methyl (CH_3-) group.

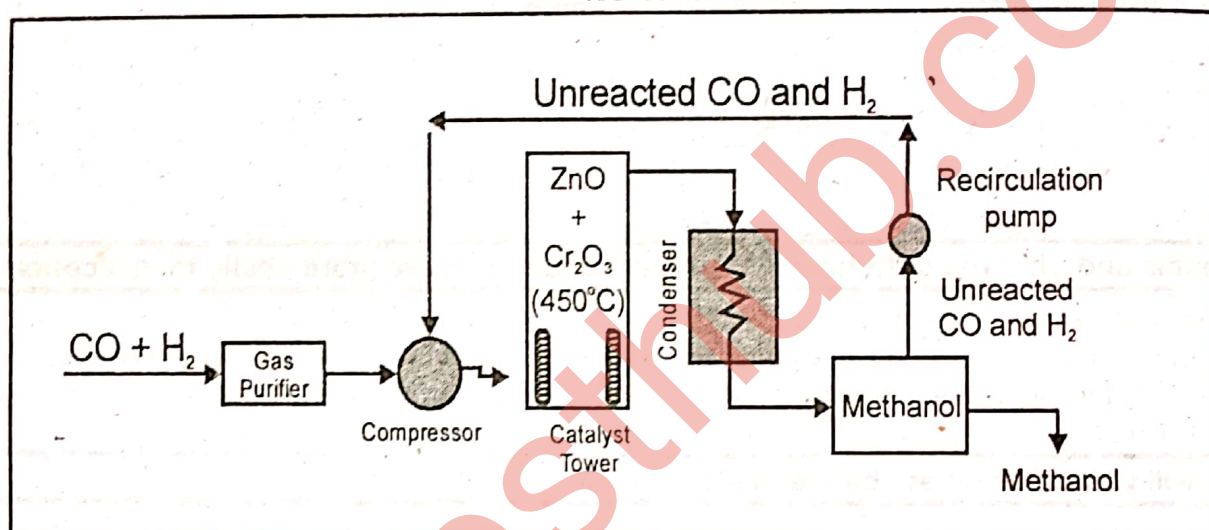
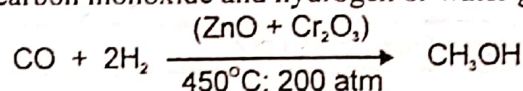


Q.3 Give detailed answers for the following questions:

Q.3(1) How will you prepare alcohols on industrial scale?

Methanol (CH_3OH)

- Formerly methanol was prepared by distillation of wood. That is why it is also called as **wood spirit**.
- Now-a-days methanol is prepared from carbon monoxide and hydrogen or water gas as follows:



Flow sheet diagram for the manufacturing of methanol

Procedure

- First of all a mixture of carbon monoxide and hydrogen is purified.
- It is compressed under a pressure of 200 atmospheres and taken into a reaction chamber by means of coiled pipes.
- Here the catalyst is heated upto $450-500^\circ C$.
- Gases react to form methanol vapours which are passed through a condenser to get methanol.
- Unreacted gases are recycled through compressor to reaction chamber.

Ethanol (C_2H_5OH)

Ethanol is prepared on industrial scale world over, by the process of fermentation.

Fermentation

It is a biochemical process which occurs in the presence of certain enzymes secreted by microorganisms such as yeast.

Necessary conditions:

- Optimum temperature for fermentation is $25-35^\circ C$.
- Proper aeration
- Dilution of solution
- Absence of any preservative

- Required temperature is $27^\circ C$
- Fermentation completes in three days
- It is an exothermic process.

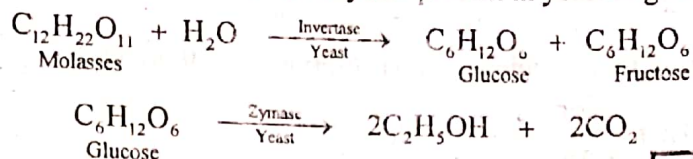
Raw Material

In Pakistan ethanol is prepared by the fermentation of molasses, starch grains or fruit juices.

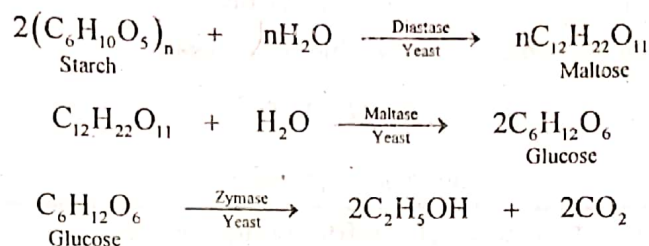
From Molasses

The residue obtained after the crystallization of sugar from concentrated sugarcane juice is called molasses.

It undergoes fermentation in the presence of enzymes present in yeast to give ethanol.



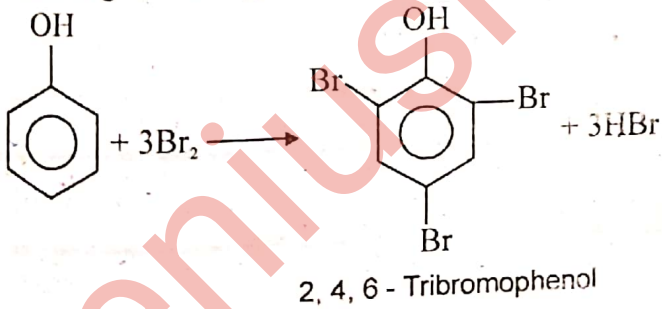
No enzyme = No fermentation

From Starch

Q.3(2) Distinguish ethanol from methanol and ethanol from phenol.

Ans.

Methanol	Ethanol
Methanol does not give iodoform test $\text{CH}_3\text{-OH} + \text{I}_2 + \text{NaOH} \longrightarrow \text{No yellow ppt}$	Ethanol gives iodoform test In iodoform test, ethanol reacts with iodine in the presence of NaOH and gives yellow coloured crystals of iodoform. $\text{CH}_3\text{-CH}_2\text{-OH} + 4\text{I}_2 + 6\text{NaOH} \longrightarrow \text{CHI}_3 + \text{HCOONa} + 5\text{NaI} + 5\text{H}_2\text{O}$

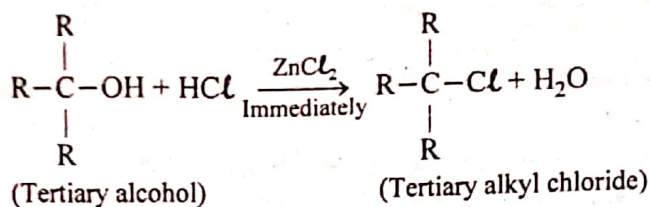
Phenol	Ethanol
An aqueous solution of phenol reacts with bromine water to give white ppt. of 2,4,6-Tribromophenol.  2, 4, 6 - Tribromophenol	An oily layer is formed when ethanol is treated with anhydrous ZnCl_2 in conc. HCl (Lucas reagent). $\text{CH}_3\text{-CH}_2\text{-OH} + \text{HCl} \xrightarrow[\text{Heat}]{\text{ZnCl}_2} \text{CH}_3\text{-CH}_2\text{-Cl} + \text{H}_2\text{O}$

Q.3(3) How will you distinguish between primary, secondary and tertiary alcohols? Explain with reactions.

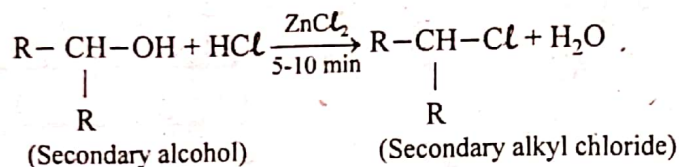
Ans. **Lucas Test**

Lucas test is used distinguish between primary, secondary and tertiary alcohols. For this purpose alcohol is treated with a solution of ZnCl_2 in concentrated HCl.

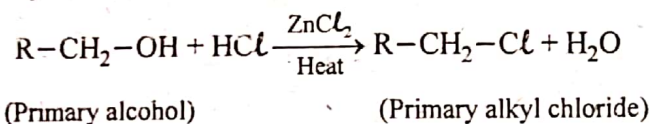
- (i) Tertiary alcohol immediately forms an insoluble iayer of a ter-alkyl chloride.



(ii) Secondary alcohol forms an insoluble sec-alkyl chloride in 5-10 minutes.



(iii) Primary alcohol forms an insoluble prim-alkyl chloride on heating.



Q.3(4) Give IUPAC names and structures of the following compounds.

(i) Sec.butyl alcohol (ii) Lactic acid (iii) ter-butyl alcohol (iv) Tartaric acid

Ans.

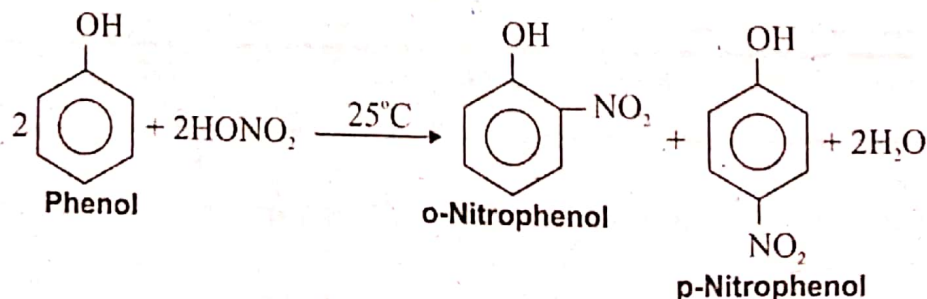
Compound	IUPAC Name	Structure
(i) Sec.butyl alcohol	2-Butanol	$\begin{array}{c} \text{CH}_3-\text{CH}_2-\text{CH}-\text{OH} \\ \\ \text{CH}_3 \end{array}$
(ii) Lactic acid	2-Hydroxypropanoic acid	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3-\text{CH}-\text{COOH} \\ \text{3} \quad \text{2} \quad \text{1} \end{array}$
(iii) ter-butyl alcohol	2-Methyl-2-propanol	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$
(iv) Tartaric acid	2,3-Dihydroxybutane-1,4-dioic acid	$\begin{array}{c} \text{HO}-\text{CH}-\text{COOH} \\ \\ \text{HO}-\text{CH}-\text{COOH} \end{array}$

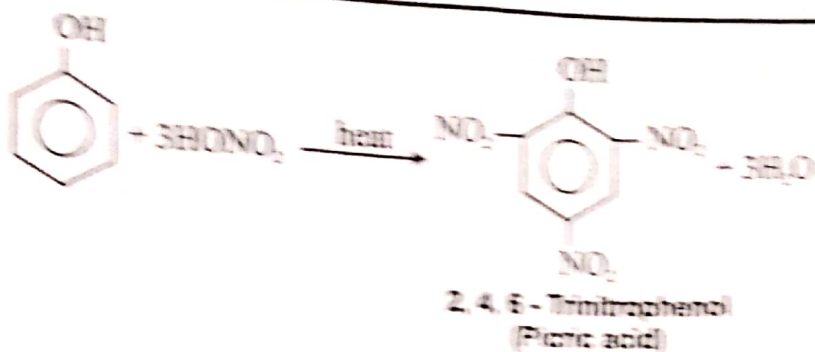
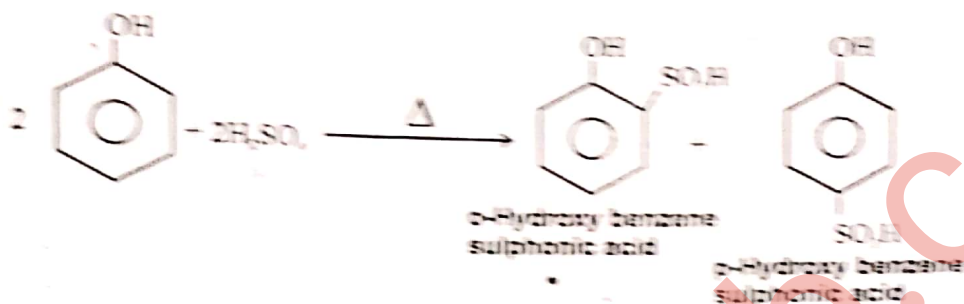
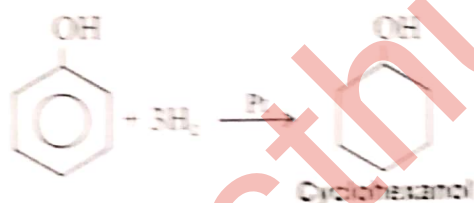
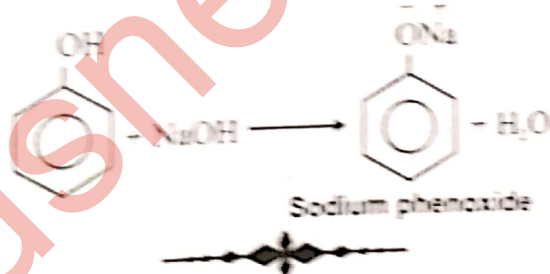
Q.3(7) How does phenol react with;

(i) HNO_3 (ii) H_2SO_4 (iii) H_2/Pt (iv) NaOH (v) Ag_2O

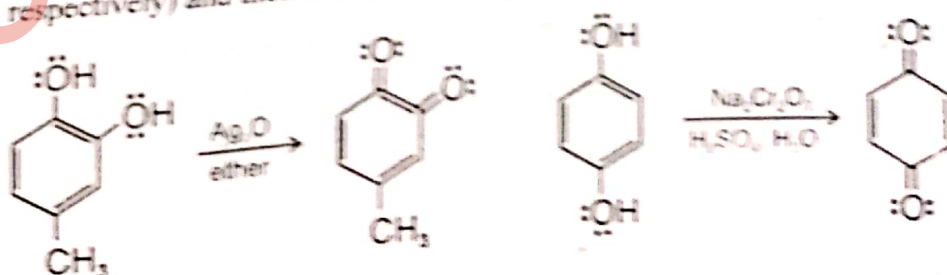
Ans. Reaction of phenol with:

(i) HNO_3



(ii) H_2SO_4 (iii) H_2/Pt (iv) NaOH (v) Ag_2O

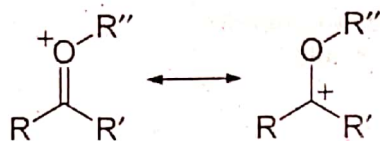
In general, phenols are more easily oxidised than simple alcohols. Oxidation can be achieved by reaction with silver oxide (Ag_2O). Particularly important are the oxidation of 1,2- and 1,4-benzenediol (pyrocatechol and hydroquinone, respectively) and their derivatives:



Q.3(8) What is oxonium ion? Describe the chemical reactivity of ether.

Ans. Oxonium ion

An oxonium ion is any oxygen cation with three bonds. The simplest oxonium ion is the hydronium ion H_3O^+ . Another class of oxonium ions is the oxocarbenium ions, obtained by protonation or alkylation of a carbonyl group e.g. $\text{R}-\text{C}=\text{O}^+-\text{R}'$.



Chemical reactivity of ether

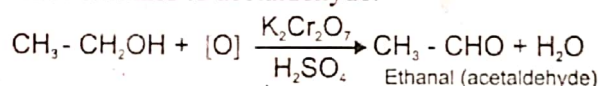
Ethers are comparatively inert substances. The reagents like ammonia, alkalis, dilute acids and metallic sodium, have no action on ethers in cold state. Moreover, they are not oxidized or reduced easily.

Q.3(9) Explain following terms using ethyl alcohol as an example;

(i) Oxidation (ii) Dehydration (iii) Esterification (iv) Ether formation

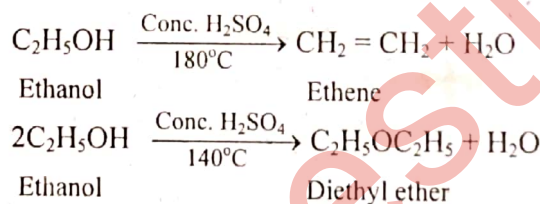
Ans. (i) Oxidation

Ethyl alcohol oxidizes to acetaldehyde.

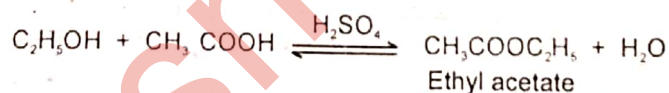


(ii) Dehydration

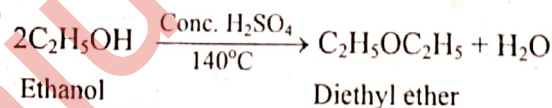
Ethyl alcohol reacts with con. H_2SO_4 and give different products at different temperatures.



(iii) Esterification



(iv) Ether formation

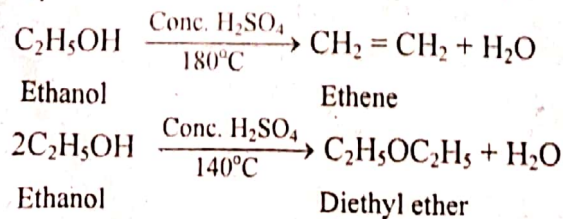


Q.3(10) How does ethyl alcohol react with the following reagents?

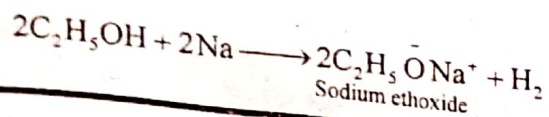
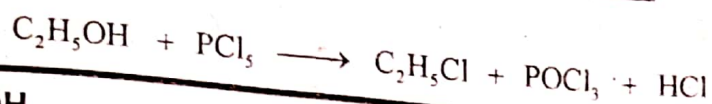
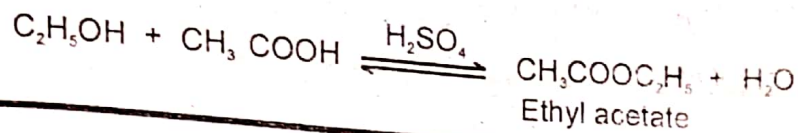
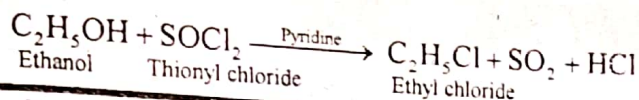
(i) Conc. H_2SO_4 (ii) Na (iii) PCl_5 (iv) CH_3COOH (v) SOCl_2

Ans. Reactions of ethyl alcohol with:

(i) Conc. H_2SO_4



(ii) Na

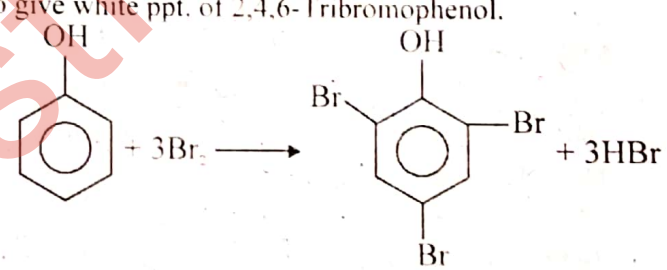
(iii) PCl_5 (iv) CH_3COOH (v) SOCl_2 

Q.3(11) How will you distinguish between?

- (i) an alcohol and a phenol
 (ii) an alcohol and an ether
 (iii) Methanol and ethanol.
 (iv) A tertiary alcohol and a primary alcohol
 (v) 1-Propanol and 2-Propanol

Ans.

(i) an alcohol and a phenol

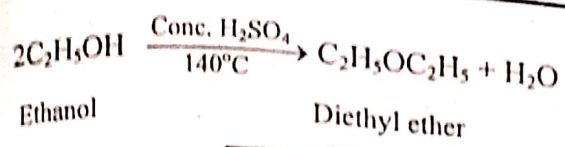
Alcohol	Phenol
An oily layer is formed when an alcohol is treated with anhydrous ZnCl_2 in conc. HCl (Lucas reagent).	An aqueous solution of phenol reacts with bromine water to give white ppt. of 2,4,6-Tribromophenol.
$\text{R}-\text{CH}_2-\text{OH} + \text{HCl} \xrightarrow[\text{Heat}]{\text{ZnCl}_2} \text{R}-\text{CH}_2-\text{Cl} + \text{H}_2\text{O}$	 <p style="text-align: center;">2, 4, 6 - Tribromophenol</p>

(ii) an alcohol and an ether

Alcohol	Ether
An oily layer is formed when an alcohol is treated with anhydrous ZnCl_2 in conc. HCl (Lucas reagent).	Ether does not form oily layer with conc. HCl and anhydrous ZnCl_2 . It means it does not give iodoform test.
$\text{R}-\text{CH}_2-\text{OH} + \text{HCl} \xrightarrow[\text{Heat}]{\text{ZnCl}_2} \text{R}-\text{CH}_2-\text{Cl} + \text{H}_2\text{O}$	$\text{R}-\text{O}-\text{R} + \text{HCl} \xrightarrow{\text{ZnCl}_2} \text{No Reaction}$

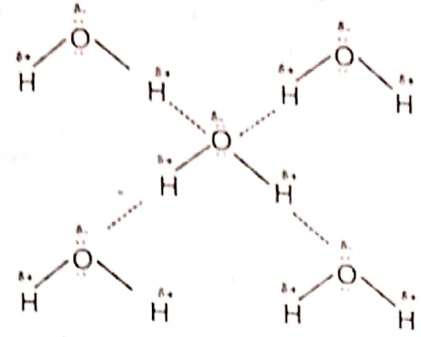
(iv) Methanol and ethanol

Methanol	Ethanol
Methanol does not give iodoform test	Ethanol gives iodoform test
$\text{CH}_3-\text{OH} + \text{I}_2 + \text{NaOH} \longrightarrow \text{No yellow ppt}$	In iodoform test, ethanol reacts with iodine in the presence of NaOH and gives yellow coloured crystals of iodoform.
	$\text{CH}_3-\text{CH}_2-\text{OH} + 4\text{I}_2 + 6\text{NaOH} \longrightarrow \text{CHI}_3 + \text{HCOONa} + 5\text{NaI} + 5\text{H}_2\text{O}$

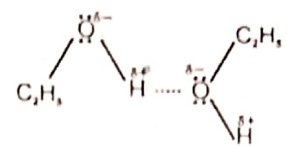


(v) **Water has higher boiling point than ethanol.**

Ans. Boiling point of a liquid depends upon strength of intermolecular forces. Stronger the intermolecular forces higher is the boiling point and vice versa.



Hydrogen bonding in water



Hydrogen bonding in ethanol

Since water can form two hydrogen bonds per molecule while ethanol can form only one hydrogen bond per molecule, therefore the extent of H-bonding in water is more than in alcohol. That's why H₂O has higher boiling point (100°C) than boiling point of ethanol (78.5°C).

Skill Activity

The two complex salts of Potassium-Ferrocyanate and Potassium-Ferricyanate are soluble in water, how will you distinguish between them by their colour?



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