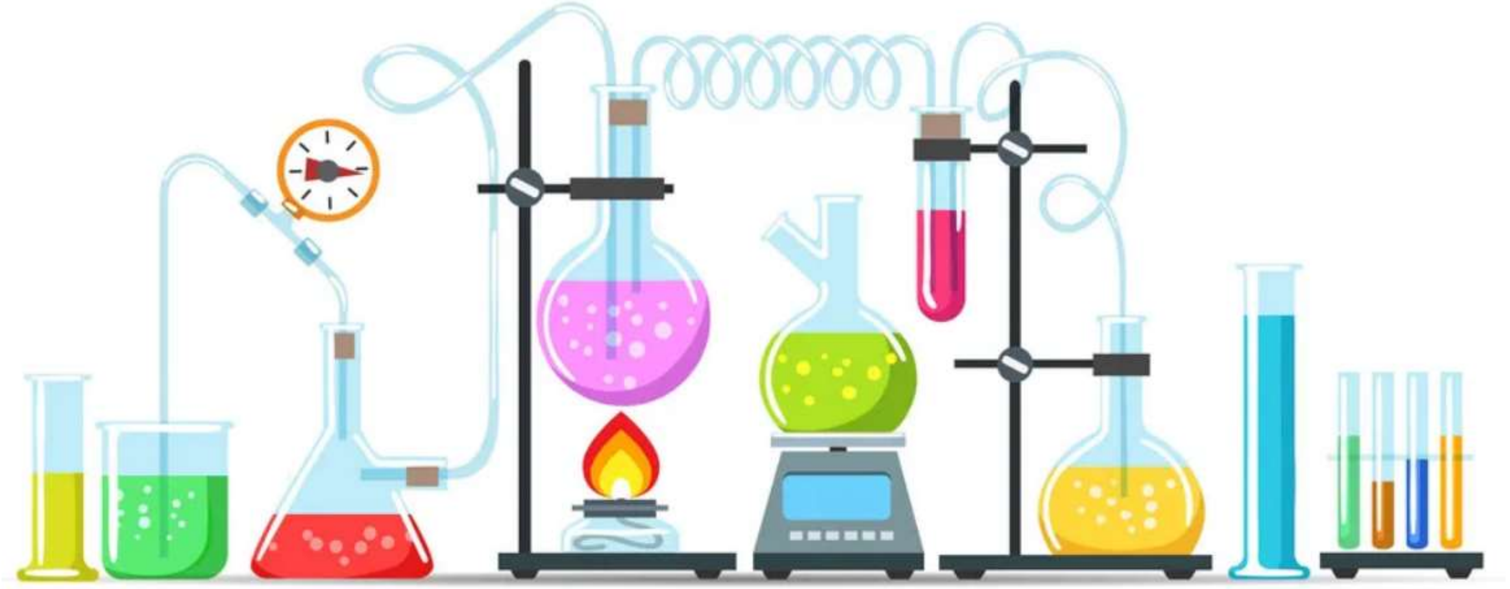
CHEMISTRY



Alcohols, Phenols and Ethers

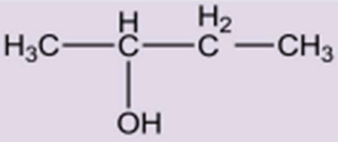
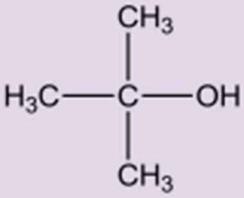
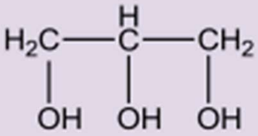
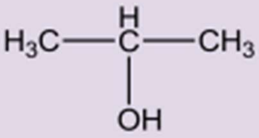
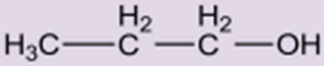
Introduction

- Alcohols and phenols are compounds formed when a hydrogen atom in a hydrocarbon is replaced by–OH group.
- An alcohol contains one or more hydroxyl (OH) group(s) directly attached to carbon atom(s) of analiphatic system.
- A phenol contains –OH group(s) directly attached to carbon atom(s) of an aromatic system (C_6H_5OH).
- The substitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group (R-O/Ar-O) givesanother class of compounds known as ethers.

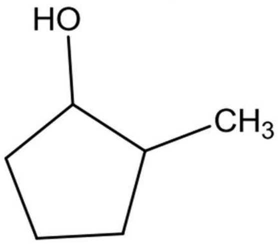
  For example:C_2H_5-O-C_2H_5 (Dimethyl ether)

Nomenclature

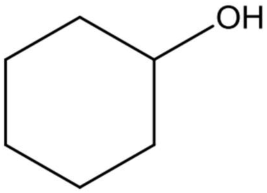
Alcohols

Compound	Common name	IUPAC name
 $H_3C-\underset{OH}{\overset{H}{C}}-\overset{H_2}{C}-CH_3$	*sec*-Butyl alcohol	Butan-2-ol
 $H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OH$	*tert*-Butyl alcohol	2-Methylpropan-2-ol
 $\underset{OH}{H_2C}-\underset{OH}{\overset{H}{C}}-\underset{OH}{CH_2}$	Glycerol	Propane -1, 2, 3-triol
 $H_3C-\underset{OH}{\overset{H}{C}}-CH_3$	Isopropyl alcohol	Propan-2-ol
 $H_3C-\overset{H_2}{C}-\overset{H_2}{C}-OH$	*n*-Propyl alcohol	Propan-1-ol

In case of cyclic compounds, we use the prefix cyclo if the –OH group is attached to C-1.

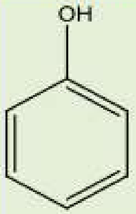
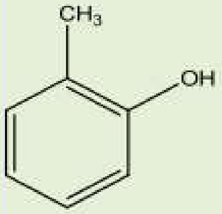
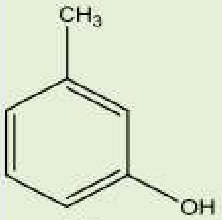
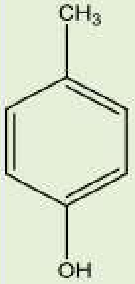
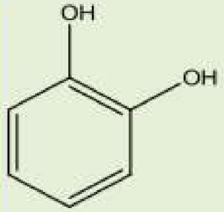
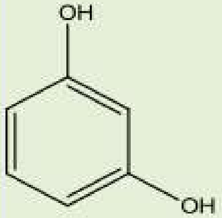
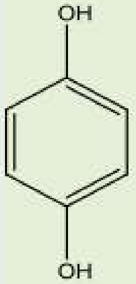


2-Methylcyclopentanol

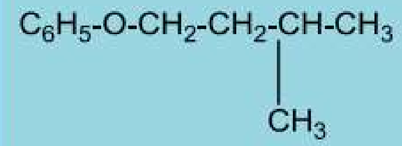
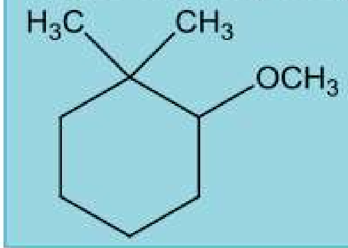


Cyclohexanol

Phenols:

Compound	Common name	IUPAC name
	Phenol	Phenol
	*o*-Cresol	2-Methylphenol
	*m*-Cresol	3-Methylphenol
	*p*-Cresol	4-Methylphenol
	Catechol	Benzene-1,2-diol
	Resorcinol	Benzene-1,3-diol
	Hydroquinone or quinol	Benzene-1,4-diol

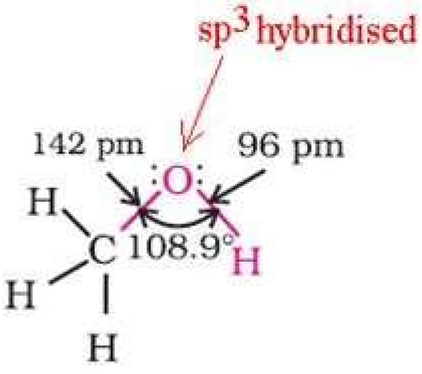
Ethers

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$C_6H_5O(CH_2)_6\text{-}CH_3$	Heptyl phenyl ether	1-Phenoxyheptane
	Phenyl isopentyl ether	3- Methylbutoxybenzene
 $C_6H_5\text{-}O\text{-}CH_2\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{\vert}{CH}}\text{-}CH_3$	----	1,2-Dimethoxyethane
$CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OCH_3$	---	
		2-Ethoxy- -1,1-dimethylcyclohexane

Structures of Functional Groups

Alcohols

- For alcohols, the –OH group is linked to carbon by a sigma bond.
- The bond is formed by the overlap of sp^3 hybridised orbital of carbon with a sp^3 hybridised orbital ofoxygen.



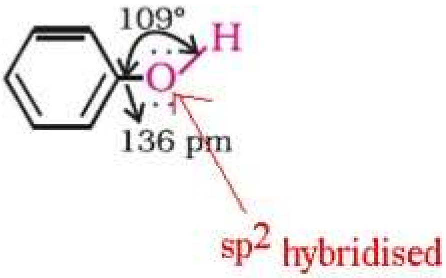
Methanol

(Alcohol)

- In alcohols, the bond angle is slightly less than the tetrahedral angle (109°-28’) due to therepulsion between the unshared electron pairs of oxygen.

Phenols

- In phenols, the –OH group is linked to carbon by sp^2 hybridisation.
- The C-O bond length (136 pm) in phenol is slightly less than that in methanol.
- This arises due to:
- ➢ Partial double bond character on account of the conjugation of unshared electron pair of oxygenwith the aromatic ring.
- ➢ sp^2 hybridised carbon to which oxygen is linked.

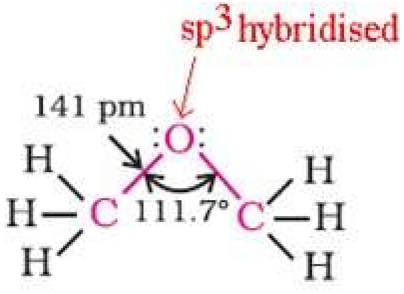


Phenol

(Phenol)

Ethers

- In ethers the two bond pairs and two lone pairs of electrons on oxygen form a tetrahedral arrangement.
- Due to the repulsive interaction between the two bulky (-R) groups the bond angle is slightlygreater than the tetrahedral angle.
- The C-O bond length is almost the same like alcohols.



Methoxymethane

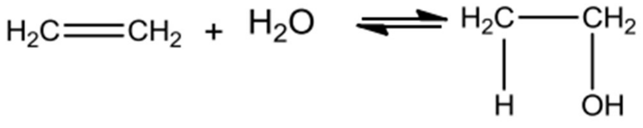
(Ether)

Preparation of Alcohols

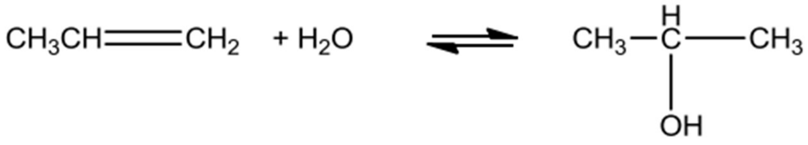
From Alkenes

- **Acid catalysed hydration:**

  Alcohols are prepared by treating alkenes with water in the presence of acid as catalyst.



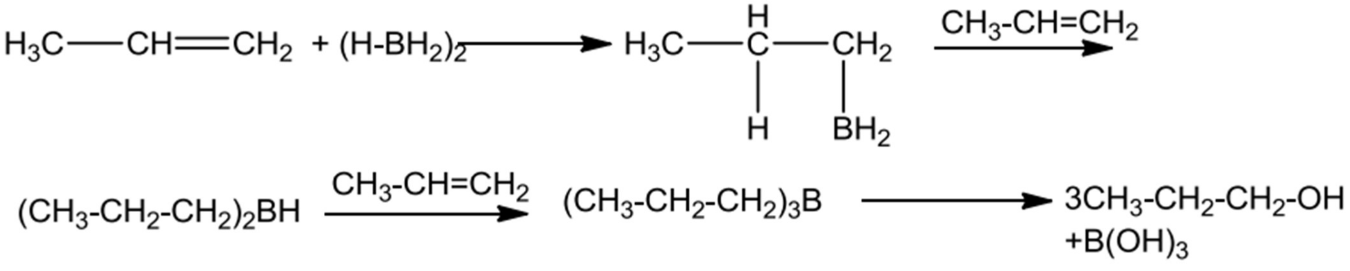
$$H_2C{=}CH_2 + H_2O \rightleftharpoons \underset{H}{\underset{|}{H_2C}}-\underset{OH}{\underset{|}{CH_2}}$$



$$CH_3CH{=}CH_2 + H_2O \rightleftharpoons CH_3-\underset{OH}{\underset{|}{\overset{H}{C}}}-CH_3$$

- **Hydroboration-oxidation:**

  Alkenes on treatment with diborane give trialkyl boranes as addition product which is then oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.



$$H_3C-CH{=}CH_2 + (H\text{-}BH_2)_2 \longrightarrow H_3C-\underset{H}{\underset{|}{\overset{H}{C}}}-\underset{BH_2}{\underset{|}{CH_2}} \xrightarrow{CH_3\text{-}CH{=}CH_2}$$

$$(CH_3\text{-}CH_2\text{-}CH_2)_2BH \xrightarrow{CH_3\text{-}CH{=}CH_2} (CH_3\text{-}CH_2\text{-}CH_2)_3B \longrightarrow 3CH_3\text{-}CH_2\text{-}CH_2\text{-}OH + B(OH)_3$$

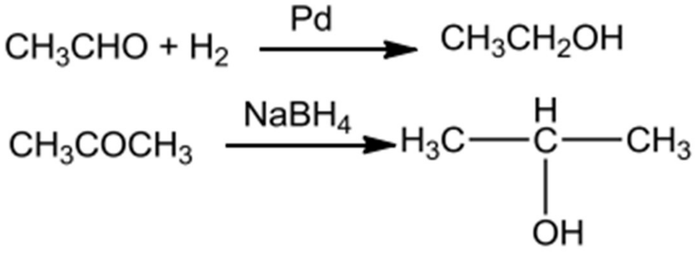
Propan-1-ol

The addition of borane to the double bond takes place in such a way that the boron gets added to thesp^2 carbon with more number of hydrogen atoms.

From Carbonyl Compounds

Reduction of Aldehydes & Ketones

- Aldehydes yield primary alcohols whereas ketones give secondary alcohols.



$$CH_3CHO + H_2 \xrightarrow{Pd} CH_3CH_2OH$$

$$CH_3COCH_3 \xrightarrow{NaBH_4} H_3C-\overset{H}{\underset{OH}{C}}-CH_3$$

Reduction of Carboxylic acids and Esters

- LiAlH$_4$ is a strong reducing agent and reduces carboxylic acids to primary alcohols in excellent yields.

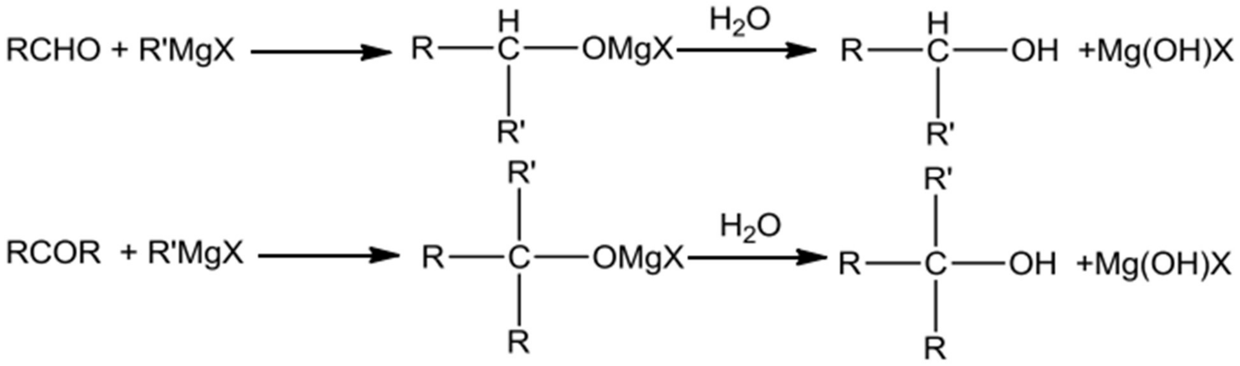
$$CH_3COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} CH_3CH_2OH$$

- Alcohols are prepared on a commercial scale by converting acids to esters followed by reduction withhydrogen in the presence of catalyst.

$$CH_3COOH \xrightarrow{CH_3OH} CH_3COOCH_3 \xrightarrow[\text{Catalyst}]{H_2} CH_3CH_2OH + CH_3OH$$

From Grignard reagents

Grignard reagents on reacting with aldehydes and ketones yield alcohols.

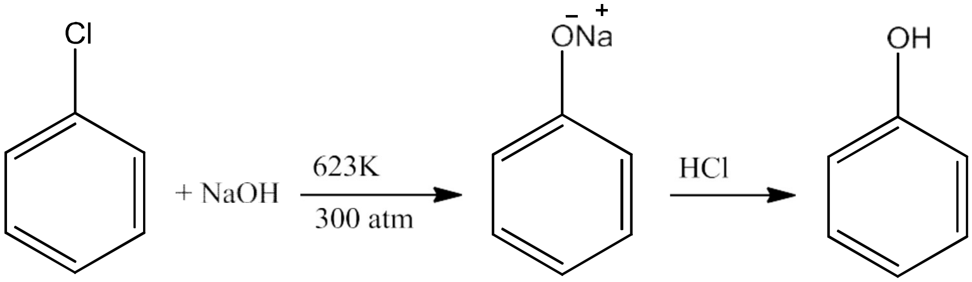


$$RCHO + R'MgX \longrightarrow R-\overset{H}{\underset{R'}{C}}-OMgX \xrightarrow{H_2O} R-\overset{H}{\underset{R'}{C}}-OH + Mg(OH)X$$

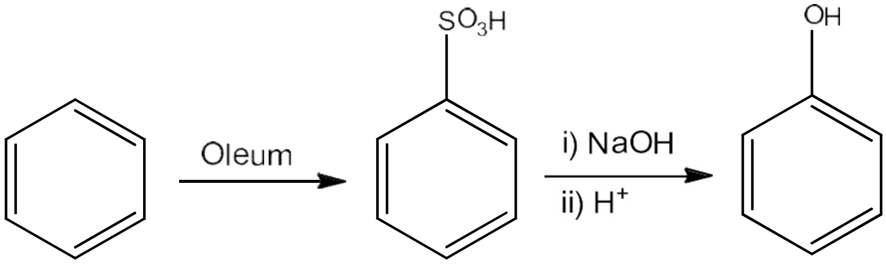
$$RCOR + R'MgX \longrightarrow R-\overset{R'}{\underset{R}{C}}-OMgX \xrightarrow{H_2O} R-\overset{R'}{\underset{R}{C}}-OH + Mg(OH)X$$

Preparation of Phenols

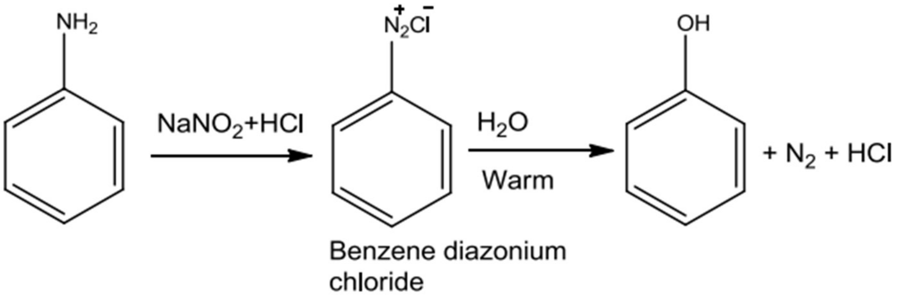
- **From Haloarenes**
  Chlorobenzene on fusing with NaOH at 623 K and 320 atmospheric pressure gives sodium phenoxidewhich on acidification yields phenol.



- **From Benzenesulphonic Acid**
  Benzene on sulphonation with oleum gives benzene sulphonic acid which on heating with moltensodium hydroxide gives sodium phenoxide. Acidification of the sodium phenoxide gives phenol.

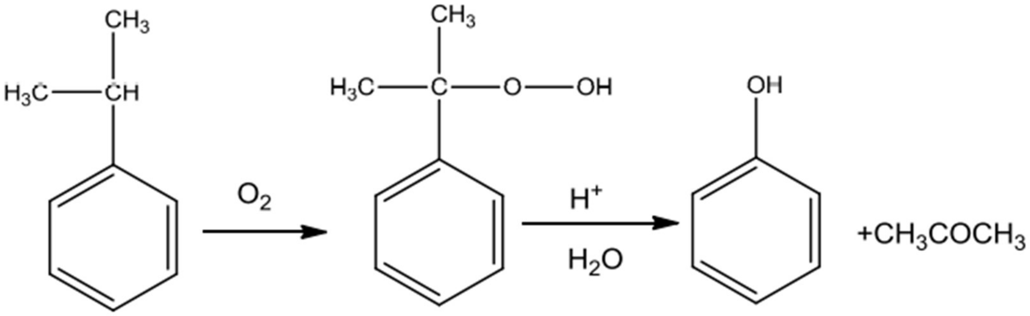


- **From Diazonium Salts**
  Aniline on treatment with nitrous acid at 273-278K gives benzene diazonium chloride which on hydrolysis with warm water or treatment with dilute acids is converted to phenols.



- **From Cumene**

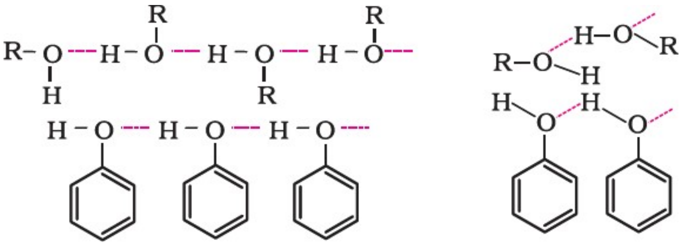
  Cumene(isopropylbenzene) on oxidation with air gives cumene hydroperoxide which on treatment withdilute acid is converted to phenol.



Physical Properties

- **Boiling points**

- Boiling points of alcohols and phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. This is because the –OH group in alcohols and phenols is involved in intermolecular hydrogen bonding.

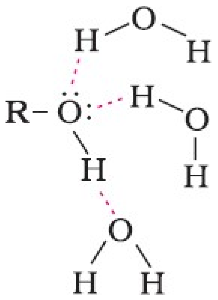


- The boiling points of alcohols and phenols increase with increase in the number of carbon atoms. This is because of increase in van der Waals forces with increase in the surface area.

- In alcohols, the boiling points decrease with increase in branching in the carbon chain. This is becauseof decrease in van der Waals forces with decrease in the surface area.

- **Solubility**

- Alcohols and phenols are soluble in water due to their ability to form hydrogen bonds with watermolecules.



- The solubility of alcohols decreases with increase in the size of alkyl/aryl (hydrophobic) groups.

Chemical Properties

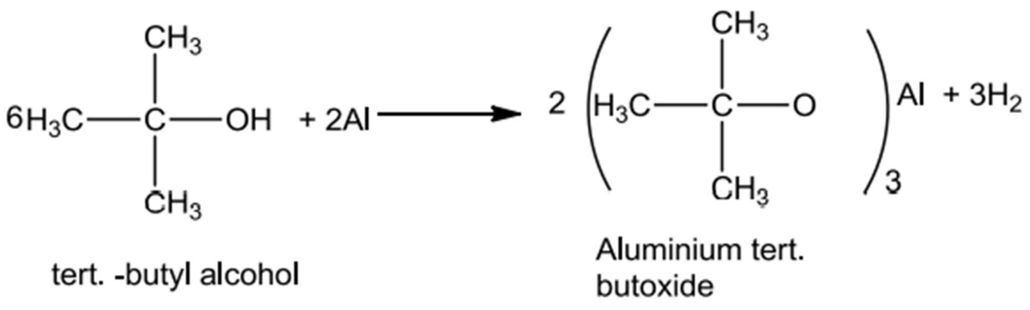
Alcohols react both as nucleophiles and electrophiles.

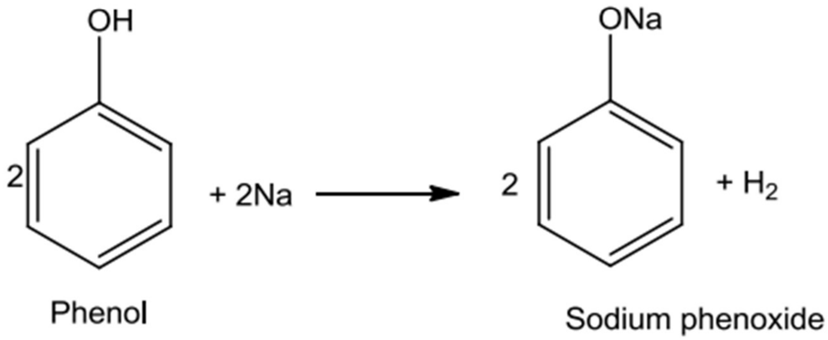
A) Reactions involving cleavage of O-H bond

(i) Reaction with Metals

Alcohols and phenols react with active metals like Na, K and Al to give correspondingalkoxides/phenoxides with the evolution of hydrogen.

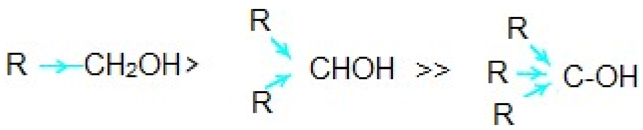
$2R\text{-}OH + 2Na \rightarrow 2R\text{-}O\text{-}Na + H_2$



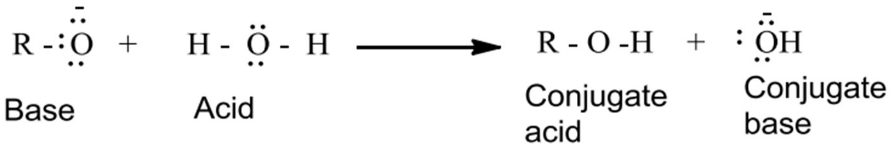


(ii) Acidity of Alcohols

- The acidity of alcohols depends on the polar nature of O-H bond.
- The electron releasing groups ($-CH_3$, $-C_2H_5$) increases the electron density on oxygen and thus decrease the polarity of O-H bond which decreases the acid strength.
- The acid strength of alcohols decreases in the following order:



- Alcohols are weaker acids than water which can be seen in the following reaction.



In the reaction, water is a better proton donor (i.e., stronger acid) than alcohol. Over herethe alkoxide ion is a better proton acceptor than hydroxide ion which suggests that alkoxides are stronger bases.

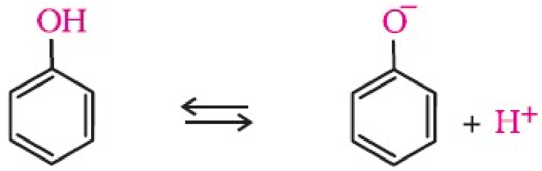
- Alcohols act as Bronsted bases as well due to the presence of unshared electron pairs onoxygen which makes them proton acceptors.

(iii) Acidity of Phenols

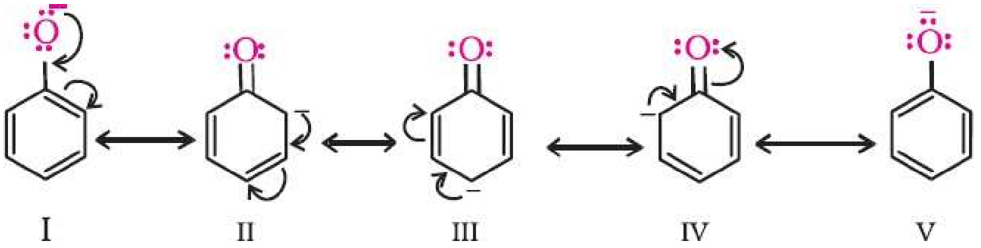
- In phenol, the hydroxyl group is directly attached to the sp^2 hybridised carbon of the benzene ring which acts as an electron-withdrawing group. Whereas in alcohols, the hydroxyl group is attached to the alkyl group which has an electron-releasing inductiveeffect.
- In phenol, the hydroxyl group is directly attached to the sp^2 hybridised carbon of the benzene ring. Whereas in alcohols, the hydroxyl group is attached to the sp^3 hybridised carbon of the alkyl group. The sp^2 hybridised carbon has higher electronegativity than the sp^3 hybridised carbon. Thus, the polarity of the O–H bond of phenols is higher than that ofalcohols. Hence, the ionisation of phenols is higher than that of alcohols.

- The ionisation of an alcohol and a phenol occurs as follows:

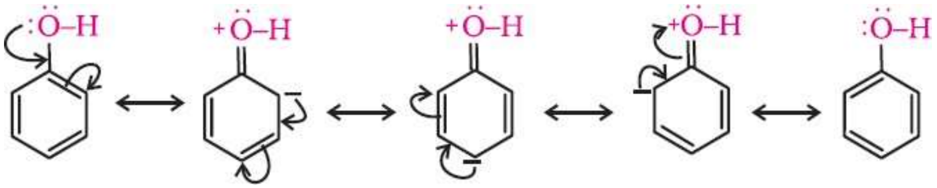
$$R-\ddot{\underset{..}{O}}-H \rightleftharpoons R-\ddot{\underset{..}{O}}{:}^{-} + H^{+}$$



- In alkoxide ion, the negative charge is localised on oxygen, while in phenoxide ion, thecharge is delocalised.



- The delocalisation of the negative charge makes the phenoxide ion more stable and favours the ionisation of phenol. Although there is charge delocalisation in phenol, its resonance structures have charge separation due to which the phenol molecule is less stable than the phenoxide ion.



- In substituted phenols, the presence of electron-withdrawing groups such as the nitro groupenhances the acidic strength of phenol. On the other hand, electron-releasing groups, suchas alkyl groups, decrease the acidic strength. It is because electron-withdrawing groups lead to effective delocalisation of the negative charge in the phenoxide ion.

(iv) Esterification

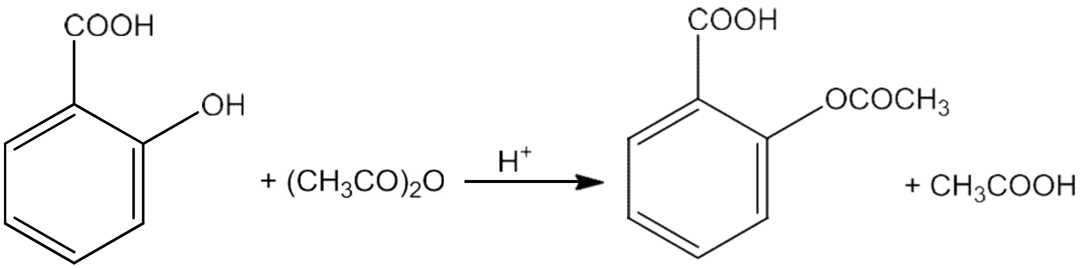
- Esters are formed when alcohols and phenols react with carboxylic acids, acid chloridesand acid anhydrides.

$$\text{Ar/RO-H} + \text{R'-COOH} \underset{}{\overset{H^{+}}{\rightleftharpoons}} \text{Ar/ROCOR'} + H_2O$$

$$\text{Ar/RO-H} + (\text{R'CO})_2\text{O} \overset{H^{+}}{\rightleftharpoons} \text{Ar/ROCOR'} + \text{R'COOH}$$

$$\text{R/ArOH} + \text{R'COCl} \xrightarrow{\text{Pyridine}} \text{R/ArOCOR'} + \text{HCl}$$

- In case of acid chloride, the reaction is carried out in the presence of base called pyridine toneutralise the HCl formed and to shift the equilibrium to the right.



Salicylic acid

Acetylsalicylic acid
(Aspirin)

B) Reactions involving cleavage of Carbon-Oxygen(C-O) bond in alcohols

Only alcohols show reactions involving cleavage of C-O bond. Phenols exhibit this type of reactiononly with zinc.

i) Reaction with hydrogen halides

Alcohols on treatment with hydrogen halides form alkyl halides.

$ROH + HX \rightarrow R\text{-}X + H_2O$

How to distinguish between Primary, Secondary and Tertiary Alcohols?

Lucas reagent test

$$ROH + HCl \xrightarrow[\text{Lucas reagent}]{\text{conc.HCl} + ZnCl_2} RCl + H_2O$$

- If it is a primary alcohol, then no turbidity appears at room temperature. Turbidity appears onlyon heating.
- If it is a secondary alcohol, then turbidity appears in 5 minutes.
- If it is a tertiary alcohol, then turbidity appears immediately.

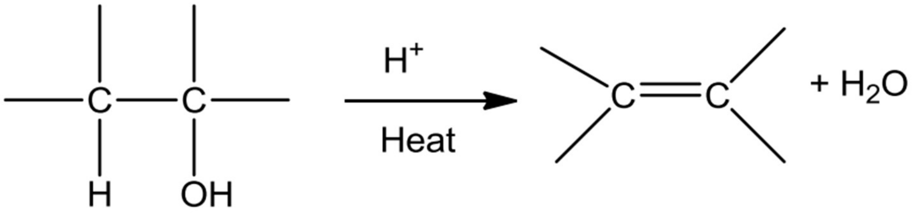
ii) Reaction with Phosphorus trihalides

Alcohols get converted into alkyl bromides on treatment with PBr_3.

$3R\text{-}OH + PBr_3 \rightarrow 3R\text{-}Br + H_3PO_3$

iii) Dehydration

- Alcohols undergo dehydration to form alkenes in the presence of conc. H_2SO_4 or H_3PO_3 orcatalysts such as anhydrous zinc chloride or alumina.

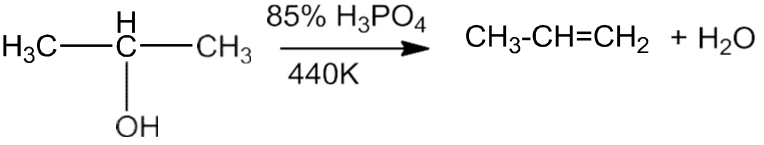


$$-\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- \xrightarrow[\text{Heat}]{H^+} >C=C< + H_2O$$

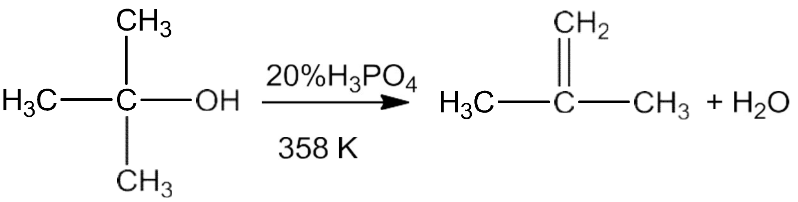
- Primary alcohol undergoes dehydration by heating it with conc. H_2SO_4 at 443K.

$$C_2H_5OH \xrightarrow[443K]{H_2SO_4} CH_2=CH_2 + H_2O$$

- Secondary and tertiary alcohols undergo dehydration in milder conditions.



$$H_3C-\underset{OH}{\overset{H}{C}}-CH_3 \xrightarrow[440K]{85\%\ H_3PO_4} CH_3\text{-}CH=CH_2 + H_2O$$

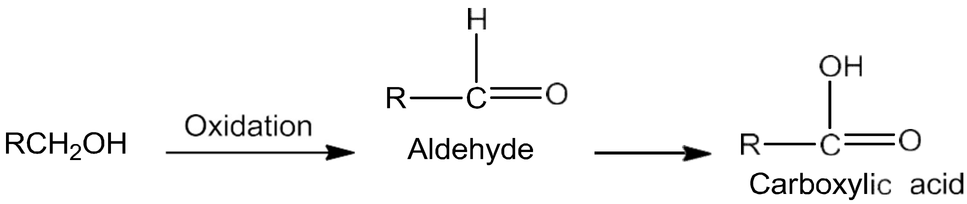


$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow[358\ K]{20\%H_3PO_4} H_3C-\overset{CH_2}{\overset{\|}{C}}-CH_3 + H_2O$$

- Thus the ease of dehydration of alcohols follows the order:
  Tertiary > Secondary > Primary

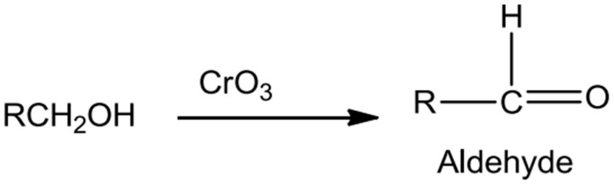
iv) Oxidation

- The oxidation of alcohols results in the formation of a carbon-oxygen double bond with the cleavage of an O-H and C-H bonds. The reaction is known as dehydrogenation reaction asit involves loss of dihydrogen from an alcohol molecule.



$$RCH_2OH \xrightarrow{\text{Oxidation}} \underset{\text{Aldehyde}}{R-\overset{H}{\overset{|}{C}}=O} \longrightarrow \underset{\text{Carboxylic acid}}{R-\overset{OH}{\overset{|}{C}}=O}$$

- Use of strong oxidising agents like acidified $KMnO_4$ is done to obtain carboxylic acids fromalcohols directly. CrO_3 in anhydrous medium is used for obtaining aldehydes.



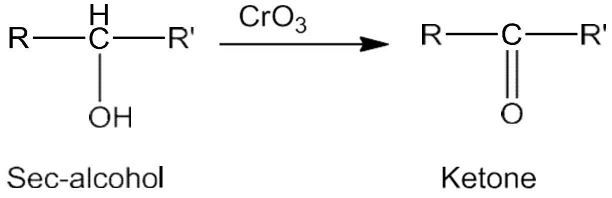
$$RCH_2OH \xrightarrow{CrO_3} \underset{\text{Aldehyde}}{R-\overset{H}{\overset{|}{C}}=O}$$

- Pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and

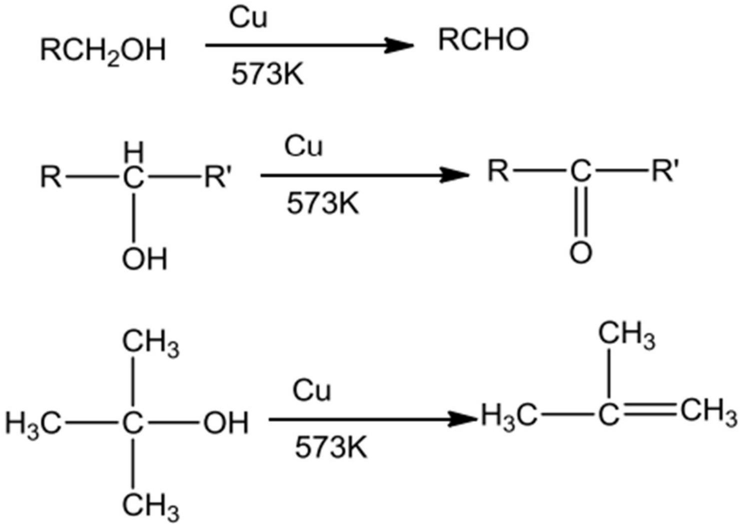
$$CH_3\text{-}CH=CH\text{-}CH_2OH \xrightarrow{PCC} CH_3\text{-}CH=CH\text{-}CHO$$

HCl isa better oxidizing agent for oxidation of primary alcohols to aldehydes in good yield.

- CrO_3 is used to oxidize secondary alcohols to ketones.



- Tertiary alcohols do not undergo oxidation reaction. In presence of strong oxidizing agents($KMnO_4$) and elevated temperatures, cleavage of C-C bonds takes place and a mixture of carboxylic acids containing lesser number of carbon atoms is formed.
- On passing vapours of a primary or a secondary alcohol over heated copper at 573K, dehydrogenation takes place and an aldehydes or a ketone is formed whereas tertiaryalcohols undergo dehydration.

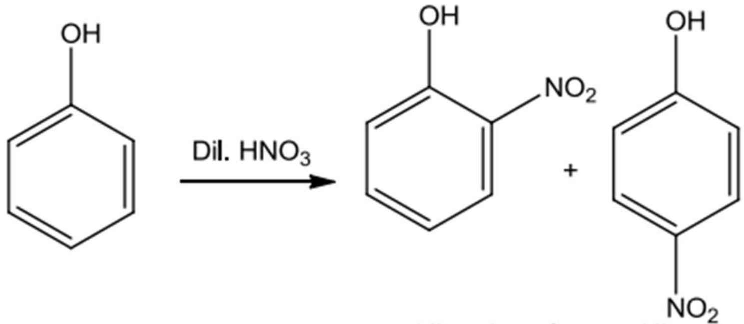


Characteristics of Phenols

- Phenols show electrophilic substitution reactions.
- The –OH group activates the benzene ring towards electrophilic substitution and also directs the incoming group to ortho and para positions in the ring as these positions become electron rich due tothe resonance effect caused by –OH group.

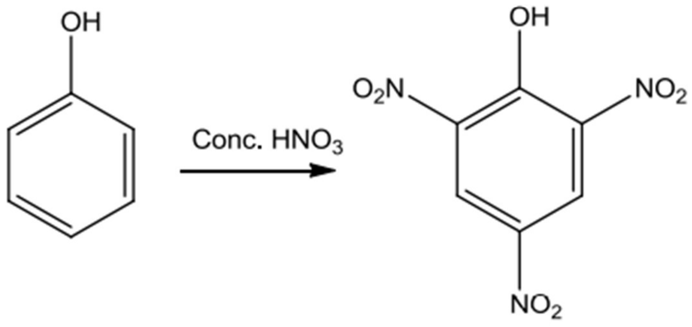
(i) Nitration

Phenol on treatment with dil.HNO_3 at low temperature yields a mixture of ortho and para nitrophenols.



o-Nitrophenol p-Nitrophenol

With conc. nitric acid, phenol is converted into 2, 4, 6-trinitrophenol.

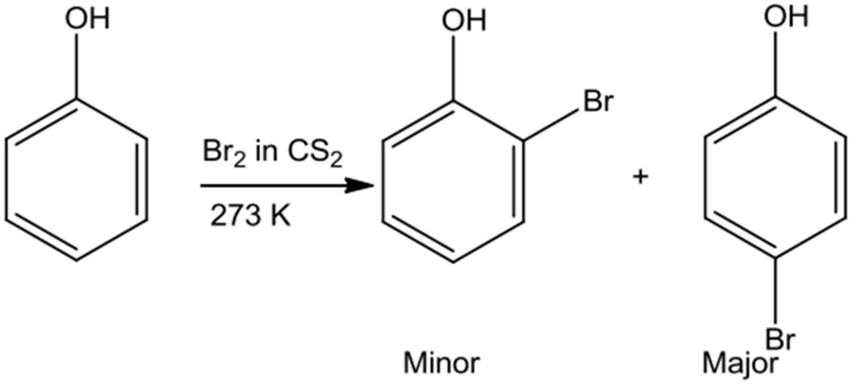


2,4,6-Trinitrophenol
(Picric acid)

(ii) Halogenation

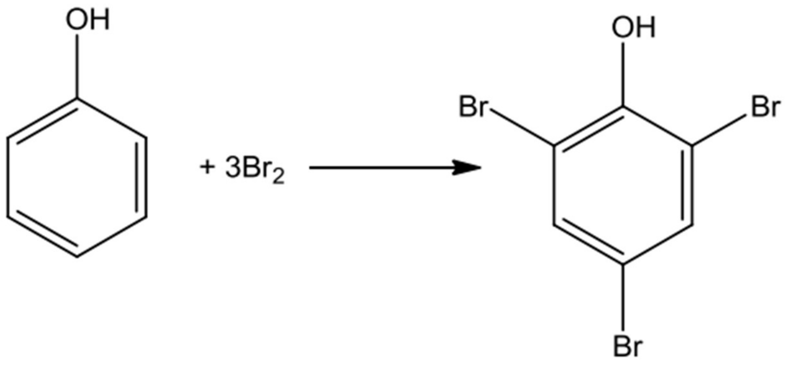
(a) Bromine in $CHCl_3$ or CS_2

Monobromophenols are formed when phenol is treated with bromine in $CHCl_3$ or CS_2 at lowtemperature.



(b) Action of Bromine water

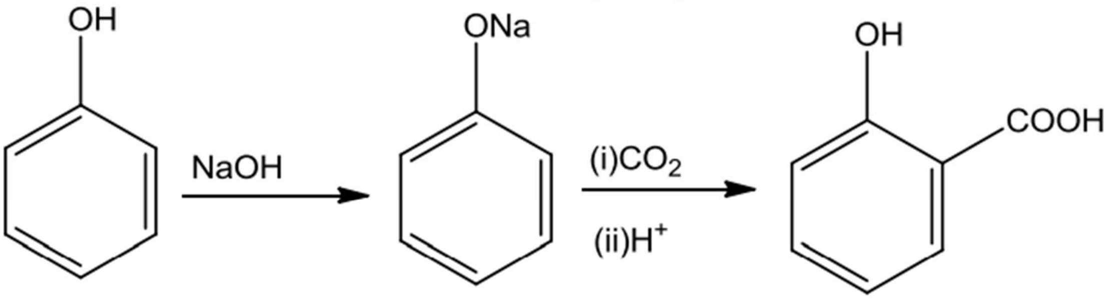
On treating phenol with bromine water, a white precipitate of 2, 4, 6-tribromophenol is formed.



2,4,6-Tribromophenol

(iii) Kolbe's Reaction

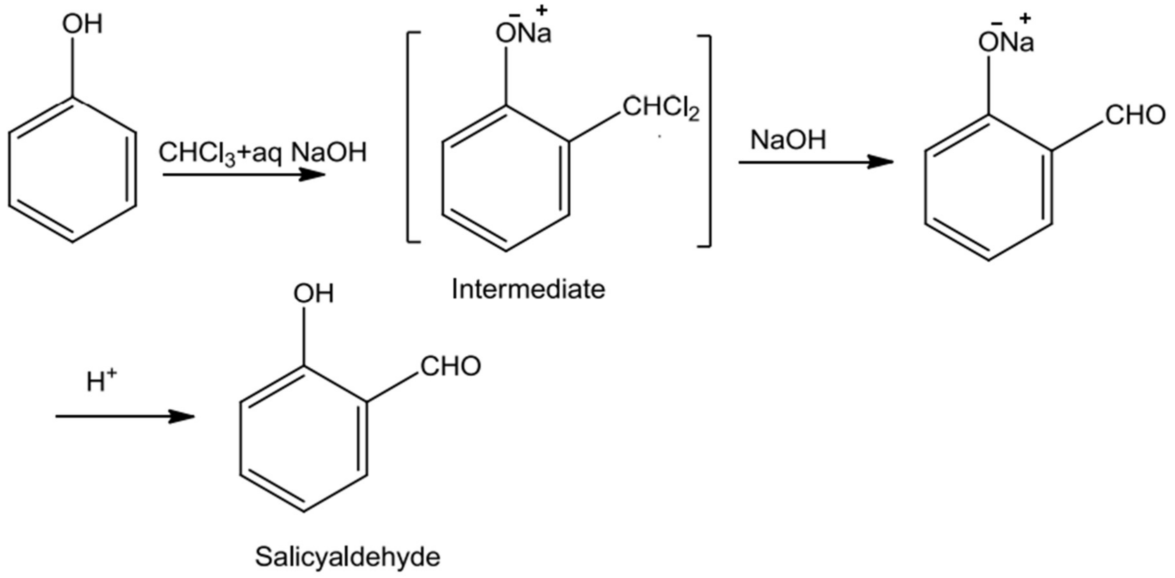
Phenols on treatment with NaOH produces phenoxide ion which is even more reactive than phenol towards electrophilic aromatic substitution and therefore it undergoes electrophilic substitution with carbon dioxide. Ortho hydroxybenzoic acid is obtained as the main product.



2-Hydroxybenzoic acid
(Salicylic acid)

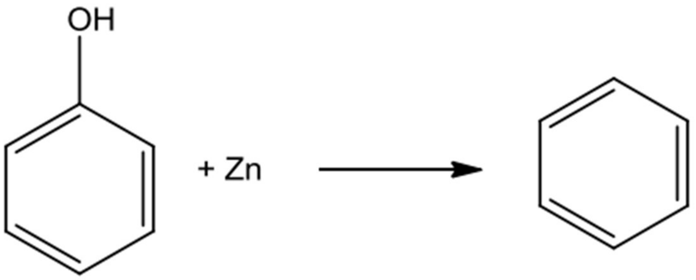
(iv) Reimer-Tiemann Reaction

Phenols on treatment with chloroform in the presence of NaOH, a –CHO group is introduced at ortho position of benzene ring. The substituted benzal chloride formed as intermediate on hydrolysis with alkali produce salicylaldehyde.



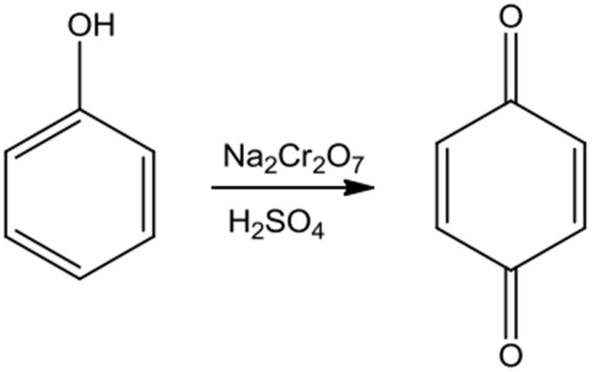
(v) Action of Zinc dust

Phenol on heating with zinc dust produces benzene.



(vi) Oxidation

Phenols on oxidation with chromic acid gives out conjugated diketone known as benzoquinone.



Some Commercially Important Alcohols

Methanol and ethanol are two commercially important alcohols.

Methanol

- Methanol also known as ‘wood spirit’ was produced by destructive distillation of wood.
- Now methanol is produced by catalytic hydrogenation of carbon monoxide at high pressure andtemperature in the presence of $ZnO\text{-}Cr_2O_3$ catalyst.

$$CO + 2H_2 \xrightarrow[\substack{200\text{-}300\ \text{atm} \\ 573\text{-}673K}]{ZnO\text{-}Cr_2O_3} CH_3OH$$

Ethanol

- It is commercially obtained by fermentation from sugars.
- The sugar in molasses, sugarcane or fruits like grapes is converted to glucose and fructose in thepresence of an enzyme invertase.
- Glucose and fructose undergo fermentation in the presence of another enzyme, zymase, which isfound in the yeast.

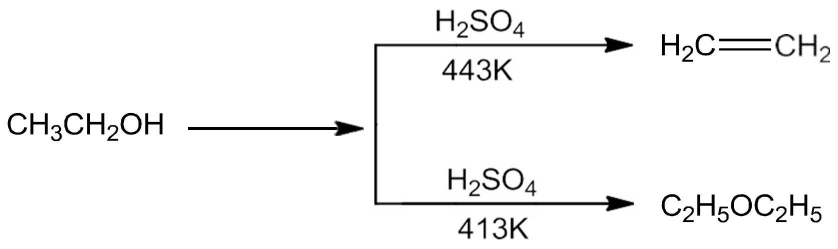
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

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

Preparation of Ethers

➢ By Dehydration of Alcohols

- Alcohols on dehydration with protic acids like H_2SO_4, H_3PO_4 give alkene or ether depending on thereaction conditions.

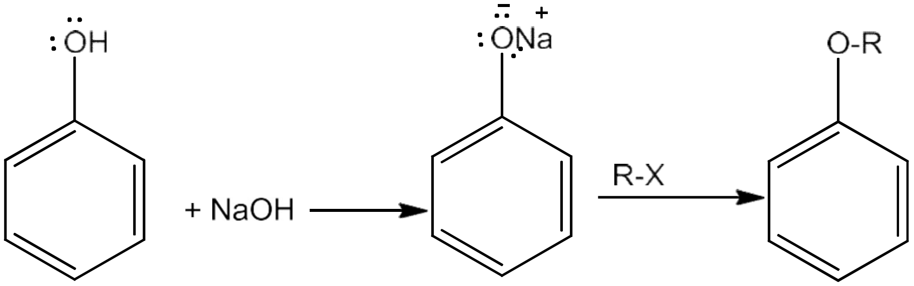


➢ Williamson Synthesis

- This method is used for the preparation of symmetrical and unsymmetrical ethers.
- In this reaction, an alkyl halide is allowed to react with sodium alkoxide.

$$R\text{-}X \quad + R'\text{-}\ddot{\underset{\cdot\cdot}{O}}{}^{-}Na^{+} \longrightarrow R\text{-}\ddot{\underset{\cdot\cdot}{O}}\text{-}R' + Na\,X$$

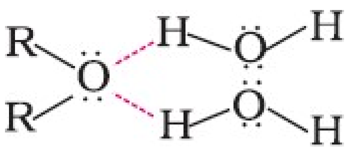
- Phenols can also be converted into ethers using this method. In this, phenol is used as thephenoxide moiety.



Physical Properties of Ethers

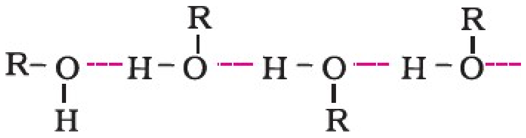
Miscibility

Miscibility of ethers with water resembles those of alcohols of the same molecular mass. This is because similar to alcohols; oxygen of ether can also form hydrogen bonds with the water molecule.



Boiling points

Ethers have much lower boiling points than alcohols. This is due to the presence of hydrogen bondingin alcohols. Hydrogen bonding is absent in ethers.



$$R-\underset{H}{O}\cdots H-\overset{R}{O}\cdots H-\underset{R}{O}\cdots H-\overset{R}{O}\cdots$$

Chemical Properties of Ethers

A. Cleavage of C–O bond in ethers

- Since ethers are least reactive of the functional groups, the cleavage of C-O bond

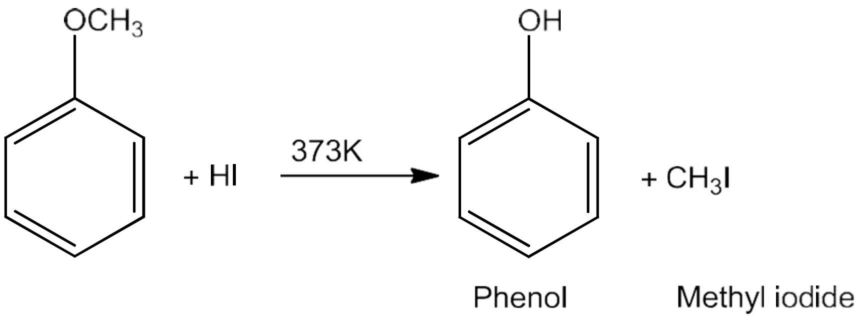
$$R\text{-}O\text{-}R + HX \longrightarrow RX + R\text{-}OH$$

in etherstakes place in excess of hydrogen halides.

- The cleavage of ethers with two different alkyl groups also takes place in the same manner.

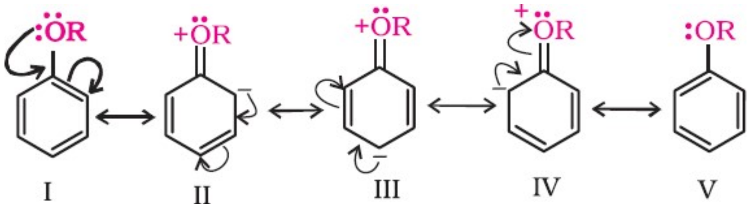
$$R\text{-}O\text{-}R' + HX \longrightarrow R\text{-}X + R'\text{-}OH$$

- In phenolic ethers, the cleavage occurs with the formation of phenol and alkyl halide.

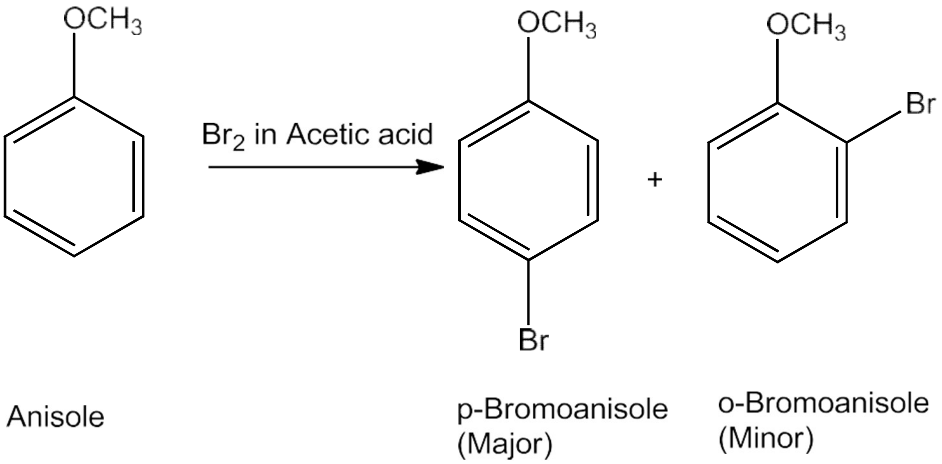


B. Electrophilic Substitution

The alkoxy group (-OR) is ortho, para directing and activates the benzene ring for aromatic substitution.



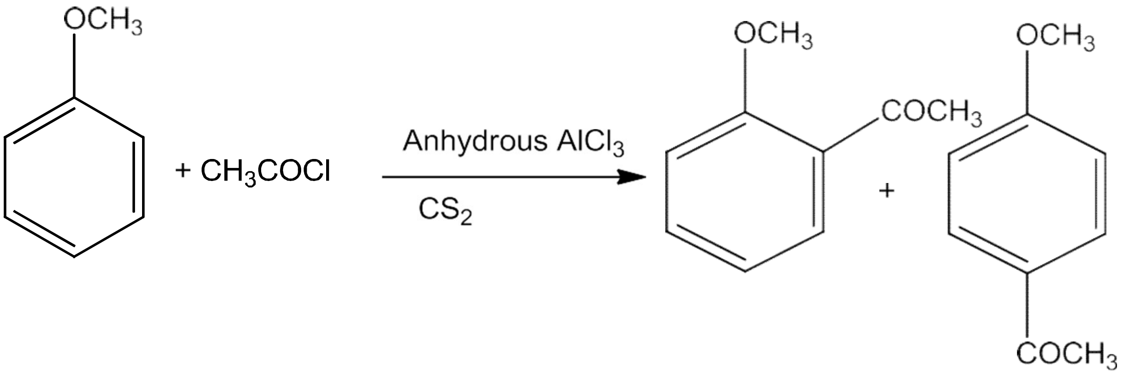
(i) Halogenation



Phenyl alkyl ethers undergo halogenation reaction.

(ii) Friedel-Crafts reaction

In this reaction the alkyl groups and acyl groups are introduced at ortho and para position by treating anisole with alkyl halide and acyl halide in the presence of anhydrous chloride ascatalyst.



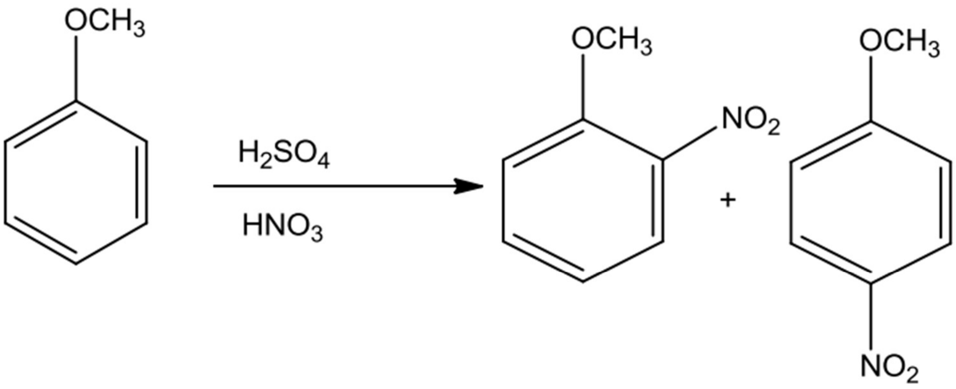
Anisole

2-Methoxy acetophenone

4-Methoxy acetophenone

(iii) **Nitration**

Anisole on treating with a mixture of sulphuric acid and nitric gives a mixture of ortho andpara nitroanisole.

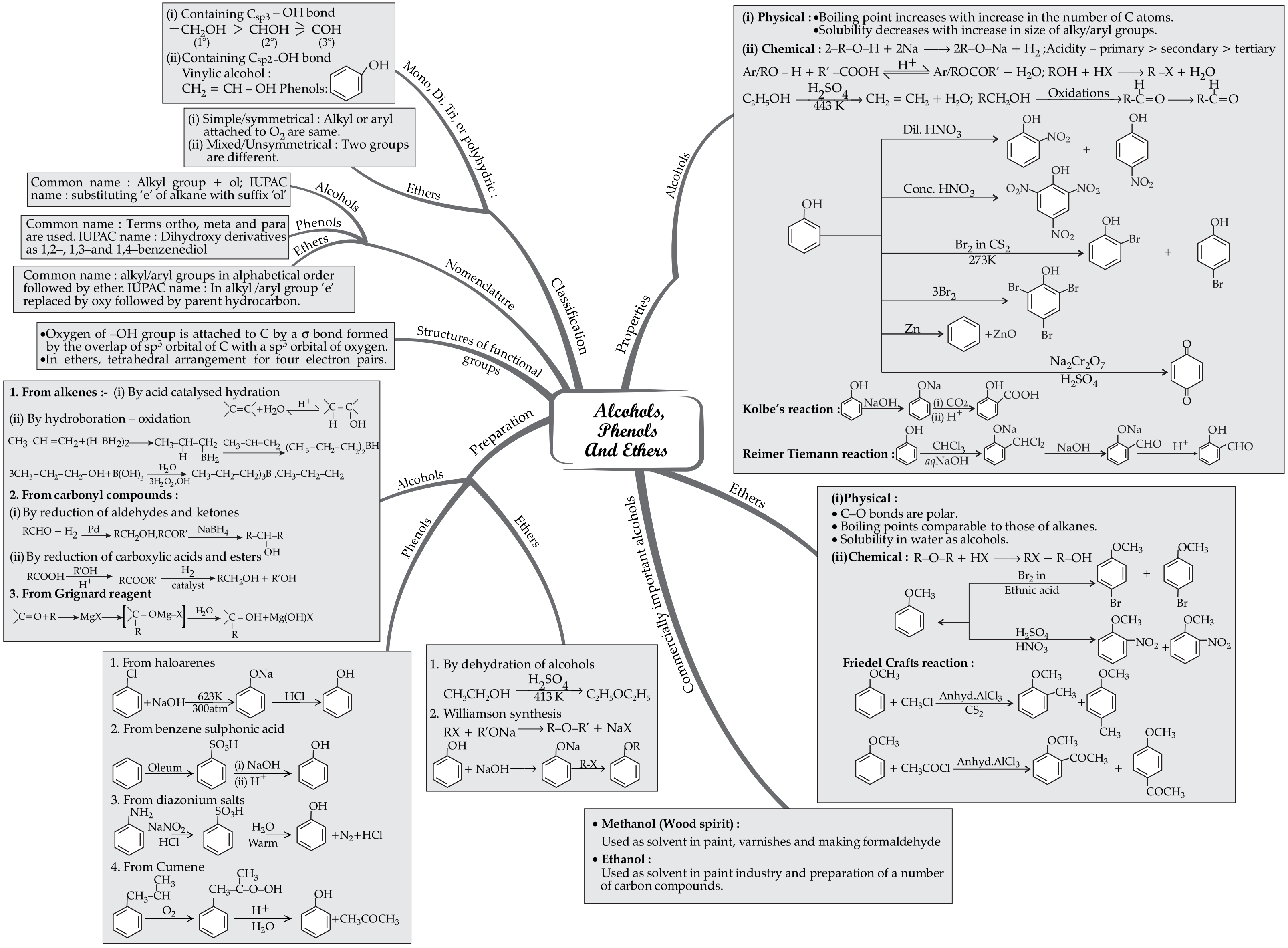


Anisole

2-Nitroanisole (Minor)

4-Nitroanisole (Major)

MIND MAP : LEARNING MADE SIMPLE CHAPTER - 11



(i) Containing C_{sp3} – OH bond

$-CH_2OH > CHOH \geqslant COH$ (1°) (2°) (3°)

(ii) Containing C_{sp2}–OH bond

Vinylic alcohol :

$CH_2 = CH – OH$ Phenols:

(i) Simple/symmetrical : Alkyl or aryl attached to O_2 are same.

(ii) Mixed/Unsymmetrical : Two groups are different.

Common name : Alkyl group + ol; IUPAC name : substituting 'e' of alkane with suffix 'ol'

Common name : Terms ortho, meta and para are used. IUPAC name : Dihydroxy derivatives as 1,2–, 1,3–and 1,4–benzenediol

Common name : alkyl/aryl groups in alphabetical order followed by ether. IUPAC name : In alkyl /aryl group 'e' replaced by oxy followed by parent hydrocarbon.

- Oxygen of –OH group is attached to C by a σ bond formed by the overlap of sp^3 orbital of C with a sp^3 orbital of oxygen.
- In ethers, tetrahedral arrangement for four electron pairs.

1. From alkenes :- (i) By acid catalysed hydration

$$>C=C< + H_2O \overset{H^+}{\rightleftharpoons} >\underset{H}{C}-\underset{OH}{C}<$$

(ii) By hydroboration – oxidation

$$CH_3–CH=CH_2+(H–BH_2)_2 \longrightarrow CH_3–\underset{H}{CH}–\underset{BH_2}{CH_2} \xrightarrow{CH_3–CH=CH_2} (CH_3–CH_2–CH_2)_2BH$$

$$3CH_3–CH_2–CH_2–OH+B(OH)_3 \xrightarrow[3H_2O_2,OH]{H_2O} CH_3–CH_2–CH_2)_3B ,CH_3–CH_2–CH_2$$

2. From carbonyl compounds :

(i) By reduction of aldehydes and ketones

$$RCHO + H_2 \xrightarrow{Pd} RCH_2OH, RCOR' \xrightarrow{NaBH_4} R–\underset{OH}{CH}–R'$$

(ii) By reduction of carboxylic acids and esters

$$RCOOH \xrightarrow[H^+]{R'OH} RCOOR' \xrightarrow[catalyst]{H_2} RCH_2OH + R'OH$$

3. From Grignard reagent

$$>C=O+R \longrightarrow MgX \longrightarrow \left[>\underset{R}{C}–OMg–X\right] \xrightarrow{H_2O} >\underset{R}{C}–OH+Mg(OH)X$$

1. From haloarenes

$+NaOH \xrightarrow[300atm]{623K}$ … $\xrightarrow{HCl}$

2. From benzene sulphonic acid

$\xrightarrow{Oleum}$ … $\xrightarrow[(ii)\ H^+]{(i)\ NaOH}$

3. From diazonium salts

$\xrightarrow[HCl]{NaNO_2}$ … $\xrightarrow[Warm]{H_2O}$ … $+N_2+HCl$

4. From Cumene

$\xrightarrow{O_2}$ … $\xrightarrow[H_2O]{H^+}$ … $+CH_3COCH_3$

1. By dehydration of alcohols

$$CH_3CH_2OH \xrightarrow[413\ K]{H_2SO_4} C_2H_5OC_2H_5$$

2. Williamson synthesis

$$RX + R'ONa \longrightarrow R–O–R' + NaX$$

$+ NaOH \longrightarrow$ … $\xrightarrow{R-X}$

(i) Physical : •Boiling point increases with increase in the number of C atoms.
•Solubility decreases with increase in size of alky/aryl groups.

(ii) Chemical : $2–R–O–H + 2Na \longrightarrow 2R–O–Na + H_2$;Acidity – primary > secondary > tertiary

$$Ar/RO – H + R' –COOH \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + H_2O; ROH + HX \longrightarrow R –X + H_2O$$

$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2 = CH_2 + H_2O; RCH_2OH \xrightarrow{Oxidations} R\text{-}\overset{H}{C}=O \longrightarrow R\text{-}\overset{H}{C}=O$$

Dil. HNO_3

Conc. HNO_3

Br_2 in CS_2 273K

$3Br_2$

Zn … +ZnO

$Na_2Cr_2O_7$ H_2SO_4

Kolbe's reaction : $\xrightarrow{NaOH}$ … $\xrightarrow[(ii)\ H^+]{(i)\ CO_2}$

Reimer Tiemann reaction : $\xrightarrow[aq NaOH]{CHCl_3}$ … $\xrightarrow{NaOH}$ … $\xrightarrow{H^+}$

(i)Physical :
- C–O bonds are polar.
- Boiling points comparable to those of alkanes.
- Solubility in water as alcohols.

(ii)Chemical : $R–O–R + HX \longrightarrow RX + R–OH$

Br_2 in Ethnic acid

H_2SO_4 HNO_3

Friedel Crafts reaction :

$+ CH_3Cl \xrightarrow[CS_2]{Anhyd.AlCl_3}$

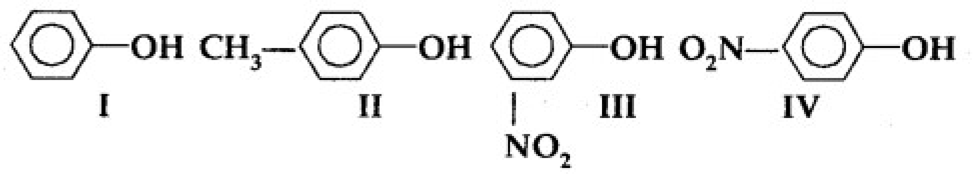
$+ CH_3COCl \xrightarrow{Anhyd.AlCl_3}$

- **Methanol (Wood spirit) :** Used as solvent in paint, varnishes and making formaldehyde
- **Ethanol :** Used as solvent in paint industry and preparation of a number of carbon compounds.

Important Questions

Multiple Choice questions-

Question 1. Among the following compounds, strongest acid is
(a) $H-C = C-H$
(b) C_6H_6
(c) C_2H_6
(d) CH_3OH
Question 2. 1-Propanol and 2-propanol can be best distinguished by
(a) Oxidation with $KMnO_4$ followed by reaction with Fehling solution?
(b) Oxidation with acidic dichromate followed by reaction with Fehling solution.
(c) Oxidation by heating with copper followed by reaction with Fehling solution.
(d) Oxidation with cone. H_2SO_4 followed by reaction with Fehling solution.
Question 3. The compound which gives the most stable carbonium ion on dehydration is
(a) $(CH_3)_2CHCH_2OH$
(b) $(CH_3)_3COH$
(c) $CH_3CH_2CH_2CH_2OH$
(d) $CH_3CH\ OH\ CH_2\ CH_3$
Question 4. In the following compounds:



The order of acidity is
(a) III > IV > I > II
(b) I > IV > III > II
(c) II > I > III > IV
(d) IV > III > I > II

Question 5. In $CH_3\ CH_2\ OH$, the bond that undergoes heterolytical change most readily is
(a) C-C
(b) C-O
(c) C-H
(d) O-H
Question 6. Phenol reacts with Br_2 in CS_2 at low temperature to give
(a) o-Bromophenol
(b) o-and p-promophenols
(c) p-Bromophenol
(d) 2, 4, 6Tribromophenol
Question 7. In the reaction of phenol with $CHCl_3$ and aqueous NaOH at 343 K, the electrophile attacking the ring is:

(a) $CHCl_3$
(b) $CHCl_2$
(c) CCl_2
(d) $COCl_2$

Question 8. Which of the following is most acidic?
(a) Phenol
(b) Benzyl alcohol
(c) m-chlorophenol
(d) cyclohexanol

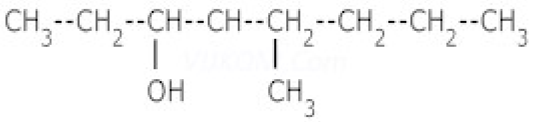
Question 9. The correct order of boiling points for primary (1°), Secondary (2°) and Tertiery (3°) alcohols is
(a) 1° > 2° > 3°
(b) 3° > 2° > 1°
(c) 2° > 1° > 3°
(d) 2° > 3° > 1°

Question 10. When Phenol is distilled with zinc dust, it gives
(a) Benzene
(b) Toluene
(c) Benzaldehyde
(d) Benzoic acid

Very Short Questions-

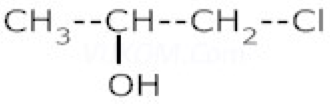
1. Write IUPAC names of :-

i.



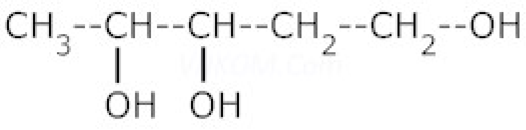
$CH_3--CH_2--\underset{OH}{\underset{|}{CH}}--\underset{CH_3}{\underset{|}{CH}}--CH_2--CH_2--CH_2--CH_3$

ii.



$CH_3--\underset{OH}{\underset{|}{CH}}--CH_2--Cl$

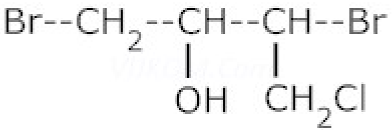
iii.



$CH_3--\underset{OH}{\underset{|}{CH}}--\underset{OH}{\underset{|}{CH}}--CH_2--CH_2--OH$

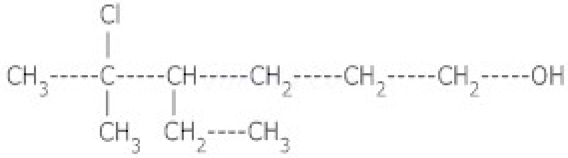
iv. $(CH_3)_3COH$

v.



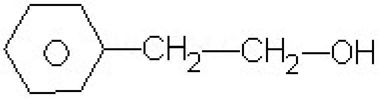
$Br--CH_2--\underset{OH}{\underset{|}{CH}}--\underset{CH_2Cl}{\underset{|}{CH}}--Br$

vi.

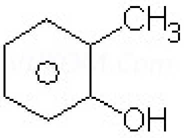


$CH_3-\overset{Cl}{\underset{CH_3}{C}}-\underset{CH_2-CH_3}{CH}-CH_2-CH_2-CH_2-OH$

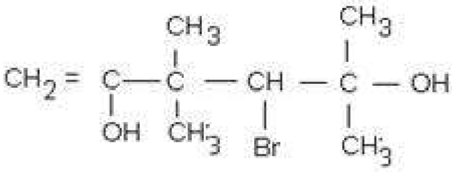
vii.



viii.

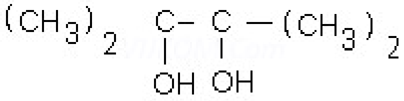


ix.



$CH_2=\underset{OH}{C}-\overset{CH_3}{\underset{CH_3}{C}}-\underset{Br}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-OH$

x.



$(CH_3)_2\ \underset{OH}{C}-\underset{OH}{C}-(CH_3)_2$

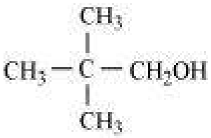
Short Questions-

1. Phenol is acidic in nature.
2. Phenol has a smaller dipole moment than methanol.
3. o- nitrophenol has lower boiling point (is more volatile) than p – nitrophenol.
4. Methanol is miscible with water while iodomethane is not.
5. Alcohols have higher boiling points than isomeric ethers.
6. Ethers are soluble in water alkanes are not.
7. The order of acidic strength in alcohols is R $CH_2OH > R_2CHOH > R_3COH$
8. During preparation of ester from alcohol and acid, water has to be removed as soon as it is formed.
9. Ethers can not be prepared by dehydration of secondary or tertiary alcohols.
10. Reaction of anisole with HI gives methyl iodide and phenol.

Long Questions-

1. Classify the following as primary, secondary and tertiary alcohols:

(i)

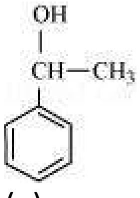


$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH$

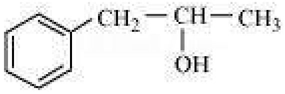
(ii) $H_2C=CH-CH_2OH$

(iii) $CH_3-CH_2-CH_2-OH$

(iv)



(v)



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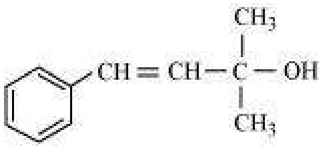
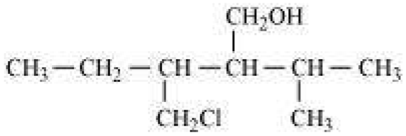


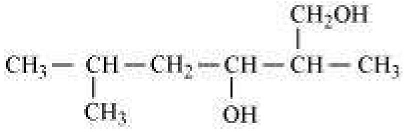
2. Name the following compounds according to IUPAC system.

(i)



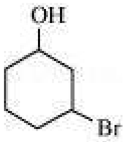
$CH_3-CH_2-\underset{CH_2Cl}{\underset{|}{CH}}-\overset{CH_2OH}{\overset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$

(ii)

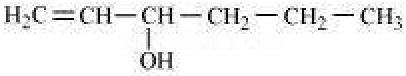


$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-\overset{CH_2OH}{\overset{|}{CH}}-CH_3$

(iii)

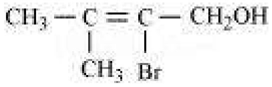


(iv)



$H_2C=CH-\underset{OH}{\underset{|}{CH}}-CH_2-CH_2-CH_3$

(v)



$CH_3-\underset{CH_3}{\underset{|}{C}}=\underset{Br}{\underset{|}{C}}-CH_2OH$

3. Give structures of the products you would expect when each of the following alcohol reacts with (a) $HCl-ZnCl_2$ (b) HBr and (c) $SOCl_2$.

(i) Butan-1-ol

(ii) 2-Methylbutan-2-ol

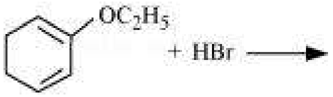
4. *Ortho* and *para* nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.

5. Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane starting from ethanol and 3-methylpentan-2-ol.

6. Predict the products of the following reactions:

(i) $CH_3-CH_2-CH_2-O-CH_3 + HBr \rightarrow$

(ii)



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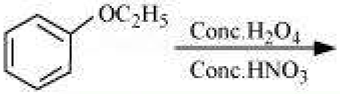
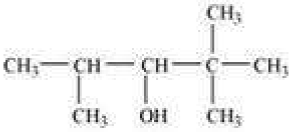


(iv) $(CH_3)_3C-OC_2H_5 \xrightarrow{HI}$

7. Write IUPAC names of the following compounds:

(i)

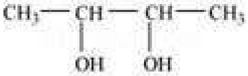


$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$

(ii)

$H_3C-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-\underset{C_2H_5}{\underset{|}{CH}}-CH_2-CH_3$

(iii)

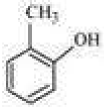


$CH_3-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_3$

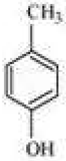
(iv)

$HO-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-OH$

(v)



(vi)



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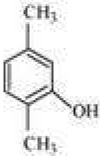
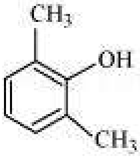
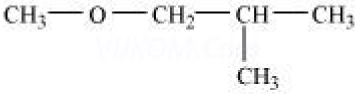


(viii)



(ix)

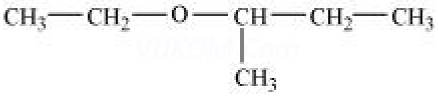


$CH_3-O-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$

(x) $C_6H_5-O-C_2H_5$

(xi) $C_6H_5-O-C_7H_{15}(n-)$

(xii)



$$CH_3-CH_2-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

8. Write structures of the compounds whose IUPAC names are as follows:

(i) 2-Methylbutan-2-ol
(ii) 1-Phenylpropan-2-ol
(iii) 3,5-Dimethylhexane -1, 3, 5-triol
(iv) 2,3 – Diethylphenol
(v) 1 – Ethoxypropane
(vi) 2-Ethoxy-3-methylpentane
(vii) Cyclohexylmethanol
(viii) 3-Cyclohexylpentan-3-ol
(ix) Cyclopent-3-en-1-ol
(x) 3-Chloromethylpentan-1-ol.

Assertion and Reason Questions-

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: Primary and secondary alcohols can be distinguished by Victor-Meyer's test.

Reason: Primary alcohols form nitrolic acid which dissolves in NaOH to form blood red colouration but secondary alcohols form pseudonitrols which give blue colouration with NaOH.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: Reimer-Tiemann reaction of phenol with $CHCl_3$ in Na OH at 340K gives salicylic acid as the major product.

Reason: The reaction occurs through intermediate formation of $^{+}CHCl_2$.

Case Study Questions-

1. Read the passage given below and answer the following questions:

An organic compound (A) having molecular formula C_6H_6O gives a characteristic colour with aqueous $FeCl_3$ solution. (A) on treatment with CO_2 and NaOH at 400K under pressure gives (B), which on acidification gives a compound (C). The compound (C) reacts with acetyl chloride to give (D) which is a popular pain killer.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Compound (A) is:

a) 2-Hexanol.
b) Dimethyl ether.
c) Phenol.
d) 2-Methyl pentanol.

(ii) Compound (C) is:

a) Salicylic acid.
b) Salicyladehyde.
c) Benzoic acid.
d) Benzaldehyde.

(iii) Number of carbon atoms in compound (D) is:

a) 7
b) 6
c) 8
d) 9

(iv) The conversion of compound (A) to (C) is known as:

a) Reimer-Tiemann reaction.
b) Kolbe's reaction.
c) Schimdt reaction.
d) Swarts reaction.

(v) Compound (A) on heating with compound (C) in presence of $POCl_3$ gives a compound (D) which is used:

a) In perfumery as a flavouring agent
b) As an antipyretic
c) As an analgesic
d) As an intestinal antiseptic.

2. Read the passage given below and answer the following questions:

A compound (X) containing C, H and O is unreactive towards sodium. It also does not react with Schiff s reagent. On refluxing with an excess of hydroiodic acid, (X) yields only one organic product (Y). On hydrolysis, (Y) yields a new compound (Z) which can be converted into (Y) by reaction with red phosphorus and iodine. The compound (Z) on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of this acid is 60.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) The compound (X) is an:

a) Acid.
b) Aldehyde.
c) Alcohol.
d) Ether.

(ii) The IUPAC name of the acid formed is:

a) Methanoic acid.
b) Ethanoic acid.
c) Propanoic acid.
d) Butanoic acid.

(iii) Compound (Y) is:

a) Ethyl iodide.
b) Methyl iodide.
c) Propyl iodide.
d) Mixture of (a) and (b).

(iv) Compound (Z) is:

a) Methanol.
b) Ethanol.

c) Propanol.
d) Butanol.

(v) Compound (X) on treatment with excess of Cl_2 in presence of tight gives:

a. ∝− Chlorodiethyl ether.
b. ∝,∝′−Dichlorodiethyl ether.
c. Perchlorodiethyl ether.
d. None of these.

MCQ Answers-

1. Answer: (d) CH_3OH

2. Answer: (c) Oxidation by heating with copper followed by reaction with Fehling solution.

3. Answer: (b) $(CH_3)_3COH$

4. Answer: (d) IV > III > I > II

5. Answer: (d) O-H

6. Answer: (b) o-and p-promophenols

7. Answer: (c) CCl_2

8. Answer: (c) m-chlorophenol

9. Answer: (a) 1° > 2° > 3°

10. Answer: (a) Benzene

Very Short Answers-

(i) **Ans.** 5 – Methyloctan-3-ol

(ii) **Ans.** 1-Chloro propan-2-ol

(iii) **Ans.** Pentan – 1,3,4 – triol

(iv) **Ans.** 2 – Methylpropan -2-ol

(v) **Ans.** 1,3 – Dibromo – 4- chloro – 2- butanol

(vi) **Ans.** 5 – Chloro – 4 – ethyl – 5- methyl hexanol.

(vii) **Ans.** 2 – Phenyl ethanol

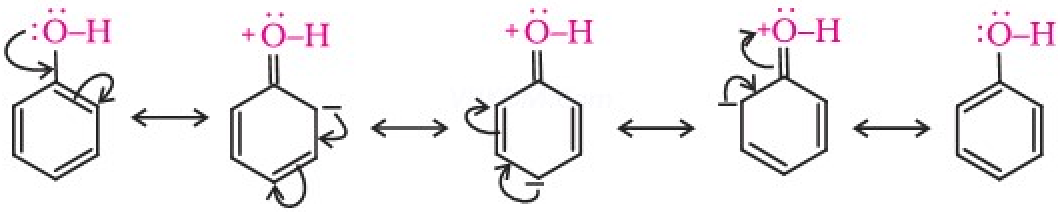
(viii) **Ans.** 2- Methyl phenol.

(ix) **Ans.** 4- Bromo -3, 3,5 – trimethyl – hex -1-ene- 2,5- diol

(x) **Ans.** 2,3 – Dimethylbutan – 2,3 –diol

Short Answers-

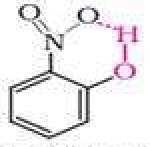
Ans 1. Phenol is acidic in nature because
(a) phenol, due to resonance, the positive charge rests on oxygen making the shared pair of electrons more towards oxygen and hydrogen as H^+



(b) The carbon attached to OH is SP^2 hybridize and is more electronegative, this decreases the electron density on oxygen, increasing the polarity of O-H bond and ionization of phenol. The phenoxide ion formed by loss of H^+ is more resonance stabilized than phenol itself.

Ans 2. In phenol due to electron rich benzene ring the C-O bond is less polar whereas in methanol the C-O bond is highly polar. Therefore the dipole moment of methanol is higher than phenol.

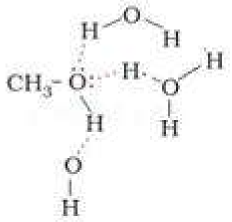
Ans 3. P- nitrophenol has intermolecular hydrogen bonding which increases the boiling point while in o- nitro phenol due to presence of intra molecular hydrogen bonding, there is a decrease in boiling point and increase in volatility.



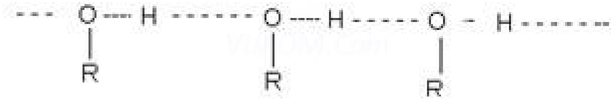
o-Nitrophenol
(Intramolecular
H-bonding)

p-Nitrophenol
(Intermolecular
H-bonding)

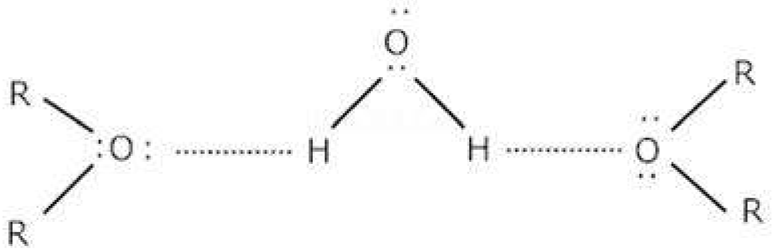
Ans 4. Methanol can form intermolecular hydrogen bonding with water but there is no hydrogen bonding in iodomethane and water. Therefore methanol in miscible in water.



Ans 5. Alcohols can form intermolecular hydrogen bonds due to their high polarity whereas, ether cannot. Therefore alcohols have higher boiling points than isomeric ethers.



Ans 6. Ethers can form H- bonding with water molecule whereas alkenes cannot. Therefore ethers are soluble in water and alkanes are not.

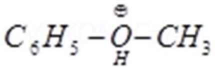


Ans 7. In alcohols, the acidic strength is due to polar nature of O-H bond. An electron releasing group e.g., alkyl groups, increases electron density on oxygen tending to decrease the polarity of O-H bond. This decreases the acid strength. Therefore the order of acid strength is .

Ans 8. The reaction between alcohol and carboxylic acid is reversible and goes in backward direction if water is not removed as soon as it is formed.

$$ROH + RCOOH \xrightleftharpoons{H^+} RCOOR' + H_2O$$

Ans 9. For secondary and tertiary alcohols, elimination competes over substitution and alkenes are formed on acidic dehydration as the reaction follows Sn1 mechanism. Therefore the acidic dehydration of secondary or tertiary alcohols does not give ethers.

Ans 10. In case of anisole, methyl phenyl oxonium ion,  $C_6H_5-\overset{\oplus}{\underset{H}{O}}-CH_3$ is formed by protonation of ethers during reaction with HI. The bond between O- CH_3 is weaker than the bond between $O-C_6H_5$ because carbon of phenyl group is SP^2 hybridised and there is a partial double bond character. Therefore the attack by I^- ion breaks $O-CH_3$ bond to form CH_3I.

$$C_6H_5\ OCH_3 + HI \rightarrow C_6H_5OH + CH_3I$$

Long Answers-

Ans 1. Primary alcohol → (i), (ii), (iii)
Secondary alcohol → (iv), (v)
Tertiary alcohol → (vi)

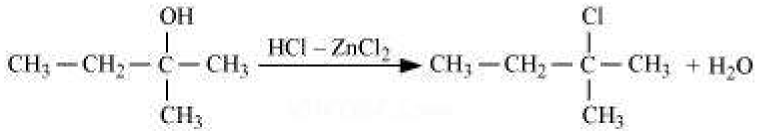
Ans 2. (i) 3-Chloromethyl-2-isopropylpentan-1-ol
(ii) 2, 5-Dimethylhexane-1, 3-diol
(iii) 3-Bromocyclohexanol
(iv) Hex-1-en-3-ol
(v) 2-Bromo-3-methylbut-2-en-1-ol

Ans 3. (a)(i)

$$\underset{\text{Butan}-1-\text{ol}}{CH_3-CH_2-CH_2-CH_2-OH} \xrightarrow{HCl-ZnCl_2} \text{No reaction}$$

Primary alcohols do not react appreciably with Lucas' reagent (HCl-ZnCl2) at room temperature.

(ii)



$$CH_3-CH_2-\overset{OH}{\underset{CH_3}{C}}-CH_3 \xrightarrow{HCl-ZnCl_2} CH_3-CH_2-\overset{Cl}{\underset{CH_3}{C}}-CH_3 + H_2O$$

2 – Methylbutan – 2 – ol (3°) 2 – Chloro – 2 – Methylbutane (White turbidity)

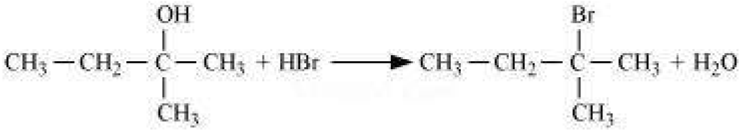
Tertiary alcohols react immediately with Lucas' reagent.

(b)

(i)

$$\underset{\text{Butan}-1-\text{ol}}{CH_3CH_2CH_2CH_2OH} + HBr \xrightarrow[-H_2O]{} \underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br}$$

(ii)



$$CH_3-CH_2-\overset{OH}{\underset{CH_3}{C}}-CH_3 + HBr \longrightarrow CH_3-CH_2-\overset{Br}{\underset{CH_3}{C}}-CH_3 + H_2O$$

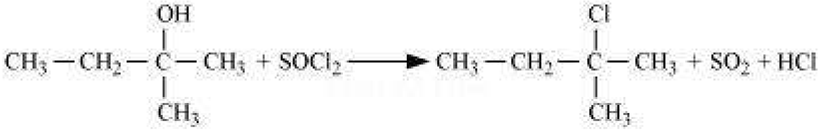
2 – Methylbutan – 2 – ol (3°) 2 – Bromo – 2 – Methylbutane

(c)

(i)

$$\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} + SOCl_2 \longrightarrow \underset{\text{1-chlorobutane}}{CH_3CH_2CH_2CH_2Cl} + SO_2 + HCl$$

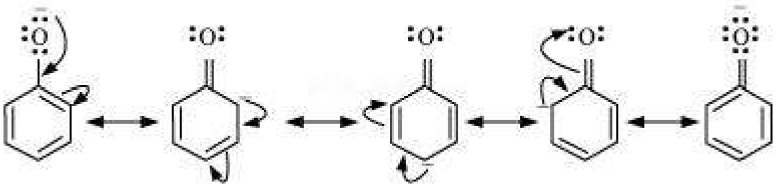
(ii)



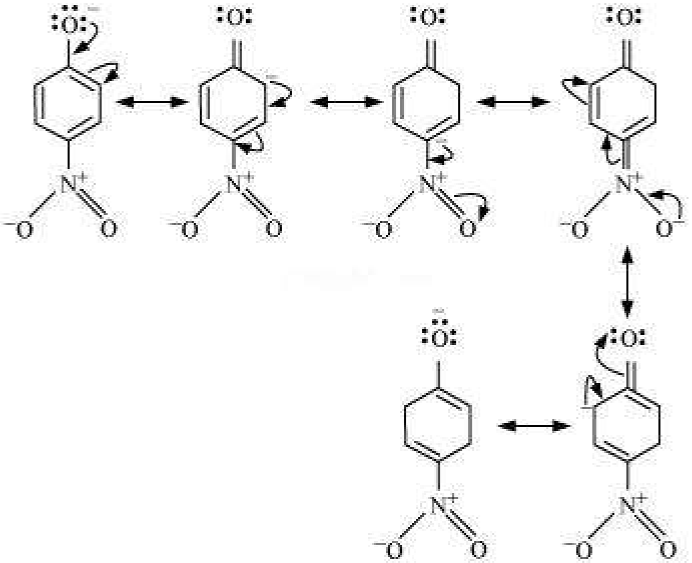
$$CH_3-CH_2-\underset{CH_3}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-CH_3 + SOCl_2 \longrightarrow CH_3-CH_2-\underset{CH_3}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}-CH_3 + SO_2 + HCl$$

2 – Methylbutan – 2 – ol 2 – Chloro – 2 – Methylbutane

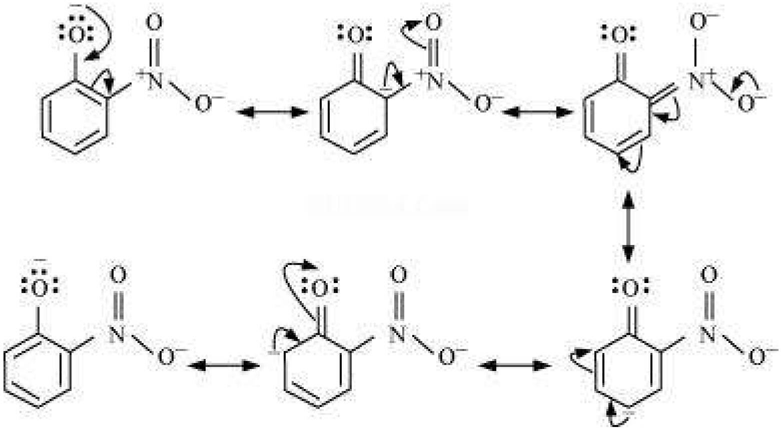
Ans 4.



Resonance structure of the phenoxide ion



Resonance structures of *p*-nitrophenoxide ion

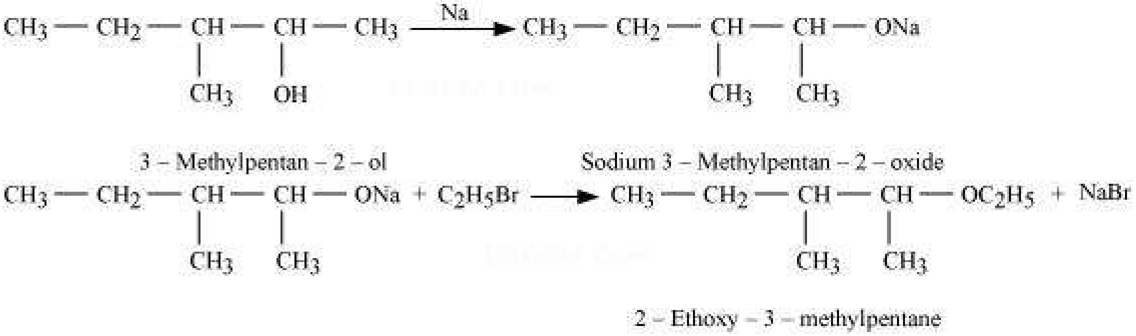


Resonance structures of *o*-nitrophenoxide ion

It can be observed that the presence of nitro groups increases the stability of phenoxide ion.

Ans 5. In Williamson synthesis, an alkyl halide reacts with an alkoxide ion. Also, it is an S_N^2 reaction. In the reaction, alkyl halides should be primary having the least steric hindrance. Hence, an alkyl halide is obtained from ethanol and alkoxide ion from 3-methylpentan-2-ol.

$$\underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow{HBr} \underset{\text{Bromoethane}}{C_2H_5Br}$$



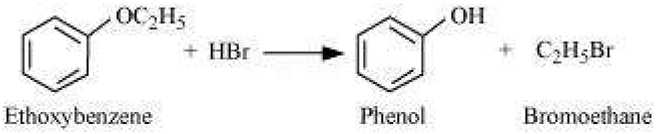
$$\underset{\text{3 – Methylpentan – 2 – ol}}{CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_3} \xrightarrow{Na} \underset{\text{Sodium 3 – Methylpentan – 2 – oxide}}{CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-ONa}$$

$$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-ONa + C_2H_5Br \longrightarrow \underset{\text{2 – Ethoxy – 3 – methylpentane}}{CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-OC_2H_5} + NaBr$$

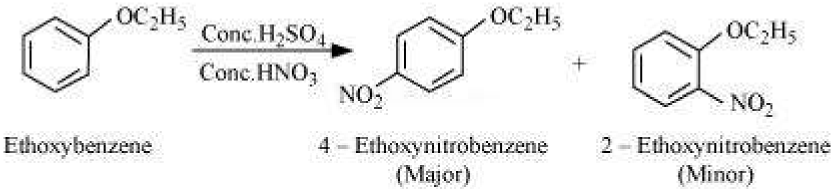
Ans 6. (i)

$$\underset{n\text{-propylmethyl ether}}{CH_3-CH_2-CH_2-O-CH_3} + HBr \longrightarrow \underset{\text{Propanol}}{CH_3-CH_2-CH_2-OH} + \underset{\text{Bromomethane}}{CH_3-Br}$$

(ii)



(iii)



(iv)

$$\underset{tert\text{-Butyl ethyl ether}}{(CH_3)_3C-OC_2H_5} \xrightarrow{HI} \underset{tert\text{-Butyliodide}}{(CH_3)_3C-I} + \underset{\text{Ethanol}}{C_2H_5OH}$$

Ans 7. (i) 2, 2, 4-Trimethylpentan-3-ol

(ii) 5-Ethylheptane-2, 4-diol

(iii) Butane-2, 3-diol

(iv) Propane-1, 2, 3-triol

(v) 2-Methylphenol

(vi) 4-Methylphenol

(vii) 2, 5-Dimethylphenol

(viii) 2, 6-Dimethylphenol

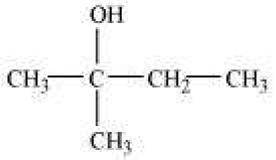
(ix) 1-Methoxy-2-methylpropane

(x) Ethoxybenzene

(xi) 1-Phenoxyheptane

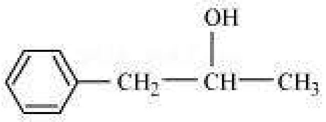
(xii) 2-Ethoxybutane

Ans 8. (i)

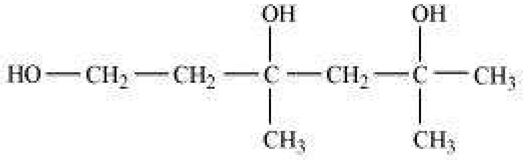


$CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2-CH_3$

(ii)

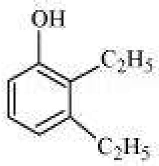


(iii)



$HO-CH_2-CH_2-\overset{OH}{\underset{CH_3}{C}}-CH_2-\overset{OH}{\underset{CH_3}{C}}-CH_3$

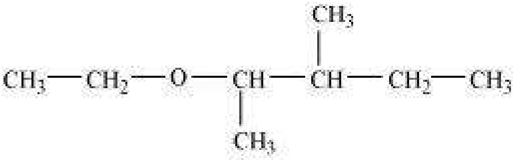
(iv)



(v)

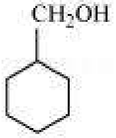
$CH_3-CH_2-O-CH_2-CH_2-CH_3$

(vi)

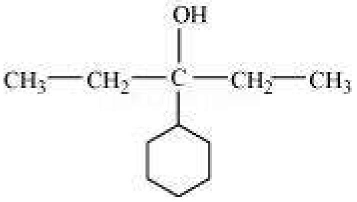


$CH_3-CH_2-O-\underset{CH_3}{CH}-\overset{CH_3}{CH}-CH_2-CH_3$

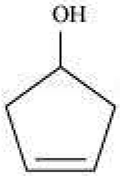
(vii)



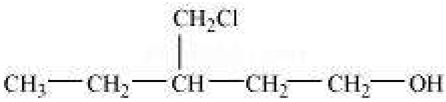
(viii)



(ix)



(x)



$CH_3-CH_2-\overset{\overset{CH_2Cl}{|}}{CH}-CH_2-CH_2-OH$

Assertion and Reason Answers-

1. (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

2. (c) Assertion is correct statement but reason is wrong statement.

Explanation:

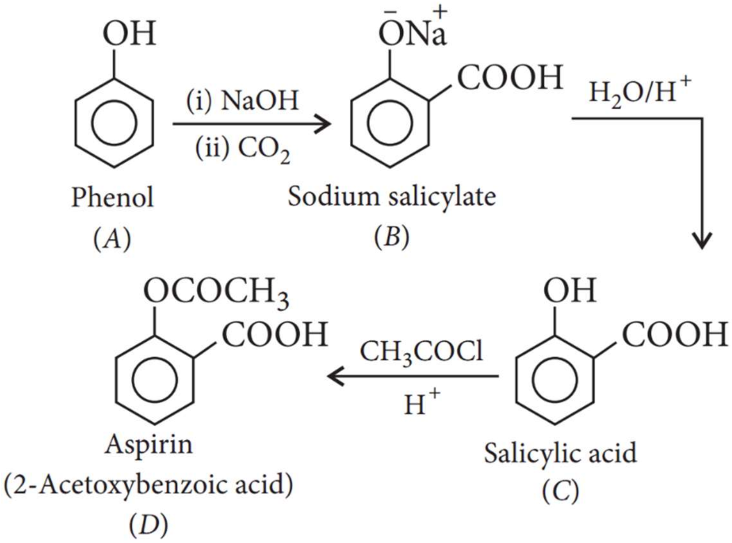
Intermediate formed is dichlorocarbene.

Case Study Answers-

1. Answer :

(i) (c) Phenol.

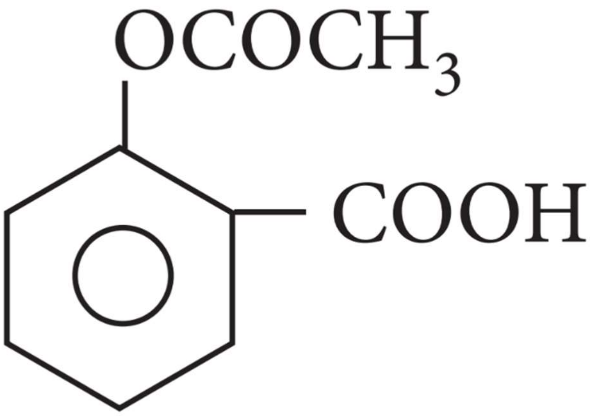
Explanation:



(ii) (a) Salicylic acid.

(iii) (d) 9

Explanation:



It has 9 C-atoms.

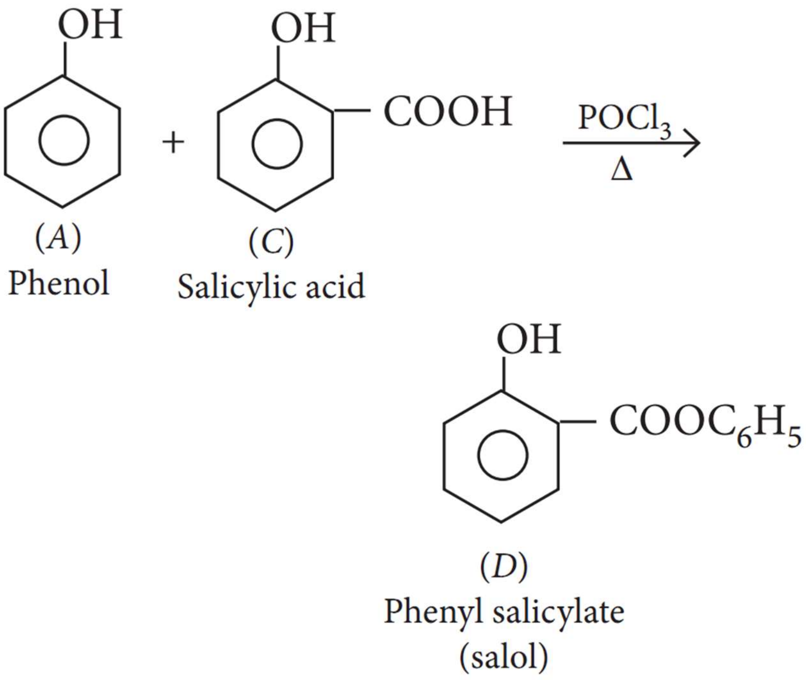
(iv) (b) Kolbe's reaction.

Explanation:

Sodium phenoxide when heated with CO_2 at 400K under a pressure of 4-7 atm followed by acidification gives 2-hydroxybenzoic acid (salicylic acid) as the main product along with a small amount of 4-hydroxybenzoic acid. This reaction is called Kolbe's reaction.

(v) (d) As an intestinal antiseptic.

Explanation:



Salol is used as an intestinal antiseptic.

2. Answer :

(i) (d) Ether.

Explanation:

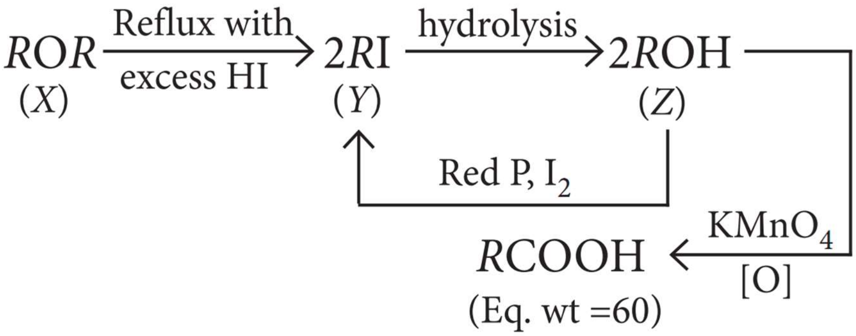
Since the compound X is unreactive towards sodium so it is neither an acid nor an alcohol. Since the compound X is unreactive towards Schiff's base so it is not an aldehyde.

The compound X forms only one product on reaction with excess HI, indicates that the compound X may be ether.

(ii) (b) Ethanoic acid.

Explanation:

The reactions can be written as:

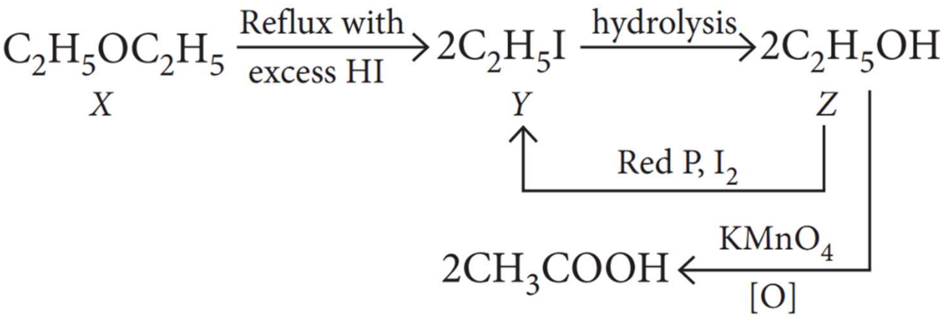


Since the equivalent weight of carboxylic acid is 60. So, it must be CH_3COOH i.e., ethanoic acid.

(iii) (a) Ethyl iodide.

Explanation:

The alcohol Z in that case should be C_2H_5OH and the compound Y should be ethyl iodide. X is therefore diethyl ether ($C_2H_5 — O — C_2H_5$)

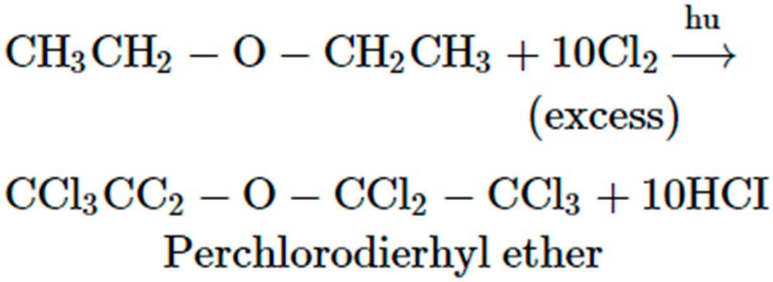


(iv) (b) Ethanol.

(v) (c) Perchlorodiethyl ether.

Explanation:

In the presence of light and excess of chlorine, all the hydrogen atoms of diethyl ether are substituted to give perchlorodiethyl ether.



$$CH_3CH_2 - O - CH_2CH_3 + \underset{\text{(excess)}}{10Cl_2} \xrightarrow{\text{hu}}$$

$$\underset{\text{Perchlorodierhyl ether}}{CCl_3CC_2 - O - CCl_2 - CCl_3} + 10HCI$$