Alcohols, Phenols and Ethers

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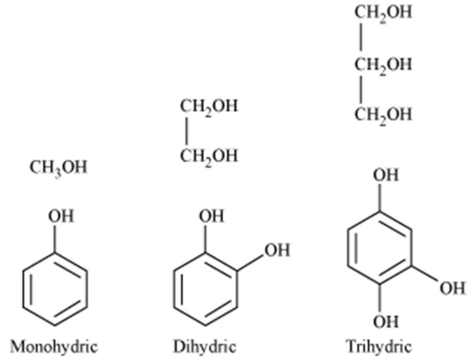
Classification and Nomenclature of Alcohols, Phenols and Ethers

Classification of Alcohols and Phenols

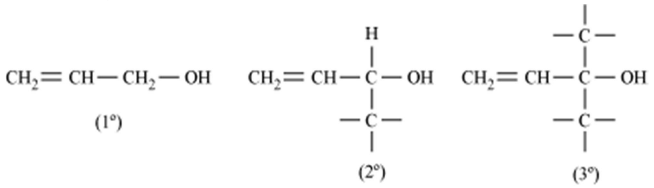
- * On the basis of number of hydroxyl groups
- * Monohydric
- * Dihydric
- * Polyhydric (tri-, tetra-, etc.)



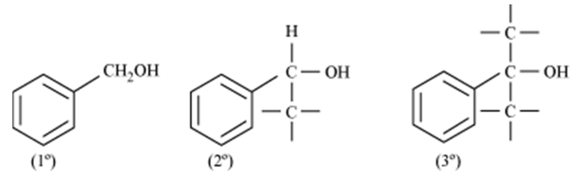
- * Monohydric alcohols are classified on the basis of hybridisation of C in C− OH bond.
- * Compounds containing C_{sp^3} − OH bond

Further classified as −

- * 1°, 2° and 3° alcohols
- * Allylic alcohols



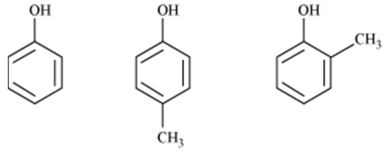
- * Benzylic alcohols



- * Compounds containing C_{sp^2} − OH bond

Further classified as −

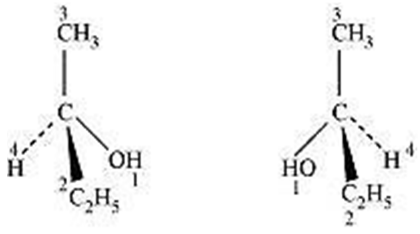
- * Vinylic alcohol
  CH_2=C− OH
- * Phenols



Solved Examples

Ex.1 Draw the three-dimensional representations of (R) - and (S) - butan- 2- ol.

Sol.



Classification of Ethers

Two categories –

Simple or symmetrical

- The two alkyl or aryl groups attached to the oxygen atom are the same.

$C_2H_5OC_2H_5$ $C_3H_7OC_3H_7$

Mixed or unsymmetrical

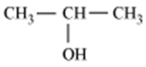
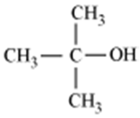
- The two alkyl or aryl groups attached to the oxygen atom are different.

$CH_3OC_3H_7$ $C_2H_5OC_6H_5$

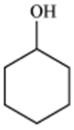
Nomenclature

Alcohols

- The common names are derived from the common name of the alkyl group, with the word alcohol added to it.
- The IUPAC names are derived by substituting 'e' of the alkane (from which the alcohol is derived) with the suffix '–ol'.
- Common and IUPAC names of some alcohols are listed in the given table.

Compound	CH_3OH	 $CH_3-\underset{OH}{CH}-CH_3$	
Common name	Methyl alcohol	Isopropyl alcohol	*tert*-Butyl alcohol
IUPAC name	Methanol	Propan-2-ol	2-Methylpropan-2-ol

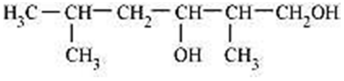
- For naming cyclic alcohols, prefix 'cyclo' is used



Cyclohexanol

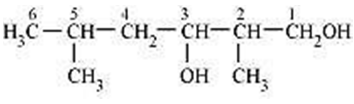
Solved Examples

Ex. 2 Write the IUPAC name of the following compound:



$H_3C-\underset{CH_3}{CH}-CH_2-\underset{OH}{CH}-\underset{CH_3}{CH}-CH_2OH$

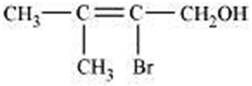
Sol.



$\overset{6}{H_3C}-\underset{CH_3}{\overset{5}{CH}}-\overset{4}{CH_2}-\underset{OH}{\overset{3}{CH}}-\underset{CH_3}{\overset{2}{CH}}-\overset{1}{CH_2}OH$

2, 5-Di-methyl-hexane-1, 3-di-ol

Ex. 3 Give the IUPAC name of the following compound:

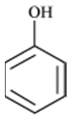
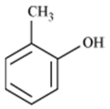
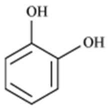
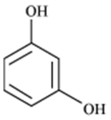
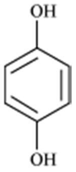


$CH_3-\underset{CH_3}{C}=\underset{Br}{C}-CH_2OH$

Sol. Bromo-3-methyl-but-2-ene-1-ol.

Phenols

- Common and IUPAC names of some phenols are given below.

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

Ethers

- The common names are derived from the alkyl or aryl groups by writing them as separate words and adding the word 'ether' at the end.
- Common and IUPAC names are listed in the given table.

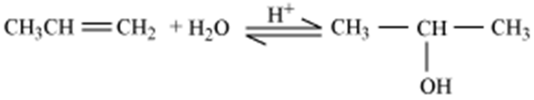
Compound	Common Name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$CH_3OCH_2CH_2CH_3$	Methyl n-propyl ether	1-Methoxypropane
$C_6H_5OCH_2CH_3$	Ethylphenyl ether	Ethoxybenzene
$C_6H_5OCH_3$	Methylphenyl ether (Anisole)	Methoxybenzene (Anisole)
$C_6H_5O(CH_2)_6 - CH_3$	Heptylphenyl ether	1-Phenoxyheptane

Methods of Preparation of Alcohols and Phenols

Preparation of Alcohols

* **From alkenes**

* By acid-catalysed hydration

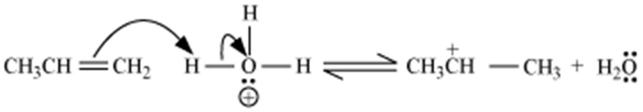


$$CH_3CH{=}CH_2 + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

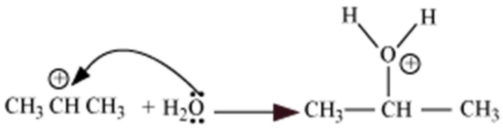
Mechanism:

Step 1 − Protonation of alkene by electrophilic attack of H_3O^+ to form carbocation

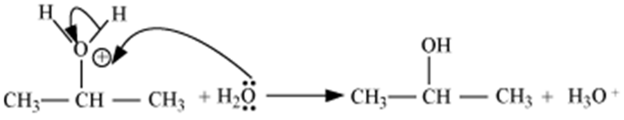
$$H_2O + H^+ \longrightarrow H_3O^+$$



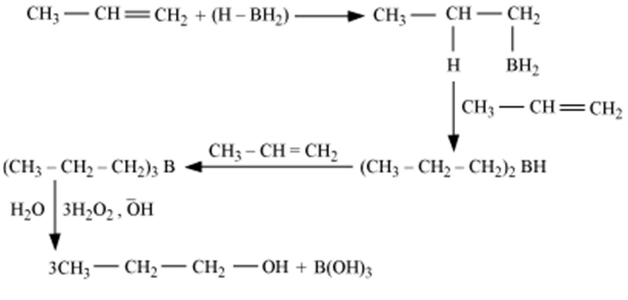
Step 2 − Nucleophilic attack of water on the carbocation



Step 3 − Deprotonation to form alcohol



* By hydroboration− oxidation



Propan-1-ol

The product so formed looks as if it were formed by the addition of water to the alkene in a way opposite to Markovnikov's rule.

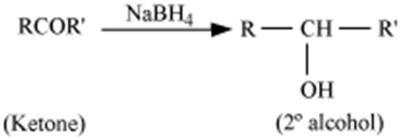
From carbonyl compounds

* By reduction of aldehydes and ketones

Catalysts →finely divided metals such as Pt, Pd or Ni, $NaBH_4$, $LiAlH_4$

Aldehydes give 1° alcohol while ketones give 2° alcohol

$$\underset{\text{(Aldehyde)}}{RCHO} + H_2 \xrightarrow{Pd} \underset{\text{(1°alcohol)}}{RCH_2OH}$$



$$\underset{\text{(Ketone)}}{RCOR'} \xrightarrow{NaBH_4} \underset{\text{(2° alcohol)}}{R-\underset{\displaystyle OH}{\underset{|}{CH}}-R'}$$

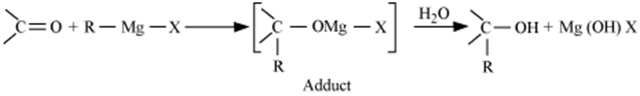
* By reduction of carboxylic acids and esters

$$\underset{\text{(Carboxylic acid)}}{RCOOH} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} \underset{\text{(1° alcohol)}}{RCH_2OH}$$

Since $LiAlH_4$ is an expensive reagent, alcohol is produced from carboxylic acid commercially in another manner.

$$\underset{\text{(Carboxylic acid)}}{RCOOH} \xrightarrow[H^+]{R'OH} \underset{\text{(Ester)}}{RCOOR'} \xrightarrow[\text{Catalyst}]{H_2} RCH_2OH + R'OH$$

* **From Grignard reagents**



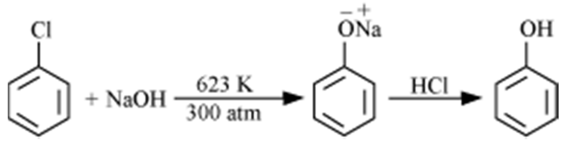
* Methanal gives 1° alcohol

* Other aldehydes give 2° alcohol

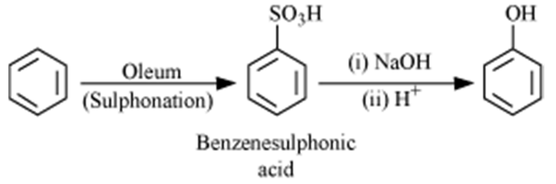
* Ketones give 3° alcohol

Preparation of Phenols (Also Known as Carbolic Acid)

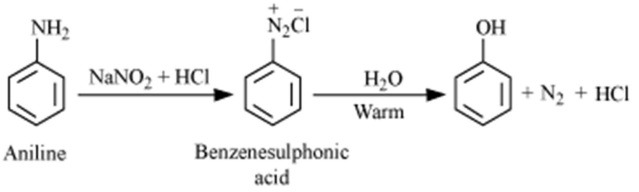
* **From haloarenes**



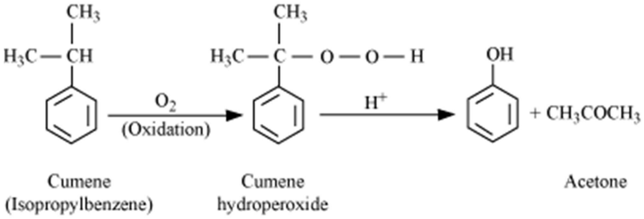
- **From benzenesulphonic acid**



- **From diazonium salts**



- **From cumene**



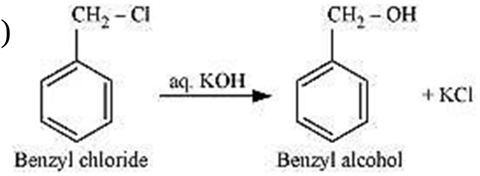
Solved Examples

Ex.4 How are the following conversions carried out?

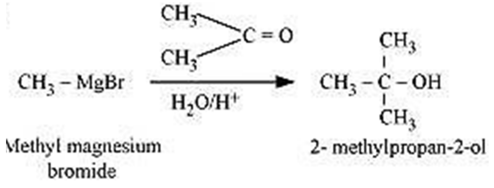
(i) Benzyl chloride to benzyl alcohol,

(ii) Methyl magnesium bromide to 2-methylpropan-2-ol

Sol. (i)



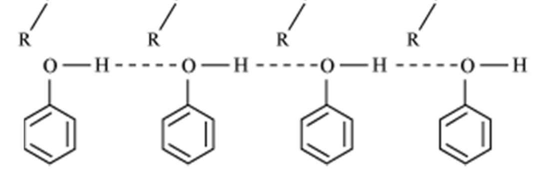
(ii)



Physical Properties of Alcohols and Phenols

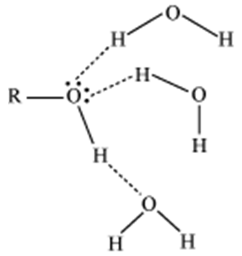
Boiling Points

- Increase with the increase in number of carbon atoms
- Reason − With the increase in the number of carbon atoms, van der Waals forces increase.
- Decrease with increase of branching
- Reason − With the increase in branching, surface area decreases and hence, van der Waals forces decrease.
- Alcohols and phenols have higher boiling points than other classes of compounds (hydrocarbons, ethers, haloalkanes, and haloarenes) of comparable molecular masses.
- Reason − They undergo extensive intermolecular hydrogen bonding resulting in aggregation of molecules.



Solubility

- **Soluble in Water**
- Reason − They undergo H-bonding with water molecules.



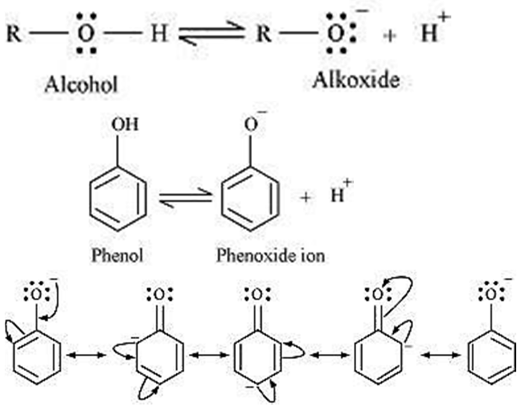
Solved Examples

Ex.5 How would you account for the following:

(i) Phenols are much more acidic than alcohols.

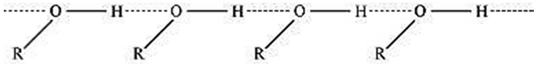
(ii) The boiling points of ethers are much lower than those of the alcohols of comparable molar masses.

Sol. (i)



Phenoxide ion is more stable than alkoxide ion due to the delocalisation of negative charge in the former. Hence, phenols are more acidic than alcohols.

(ii) Alcohols undergo intermolecular H-bonding while ethers do not.



Therefore, extra energy is required to break the H-bonds in alcohol. Hence, the boiling point of ethers is much lower than those of the alcohols of comparable molar masses.

Ex.6 Name a substance that can be used as an antiseptic as well as a disinfectant.

Sol. Phenol can be used as an antiseptic as well as a disinfectant. 0.1% solution of phenol is used as an antiseptic and 1% solution of phenol is used as a disinfectant.

Ex.7 Name the reagents which are used in the following conversions:

(i) A primary alcohol to an aldehyde

(ii) Butan-2-one to butan-2-ol

(iii) Phenol to 2, 4, 6-tribromophenol

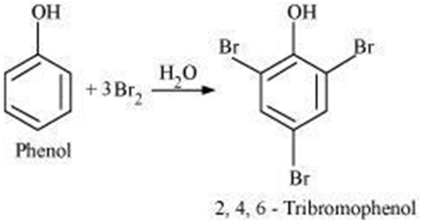
Sol. (i) Pyridinium chlorochromate (PCC) a complex of chromium trioxide with pyridine and HCl.

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

$KMnO_4$ and CrO_3 can also be used for the same.

(ii) Ni/H_2 or $LiAlH_4$ or $NaBH_4$

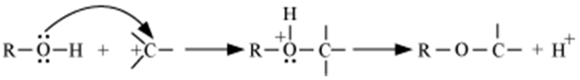
(iii) Aqueous bromine or bromine water



Chemical Reactions of Alcohols and Phenols

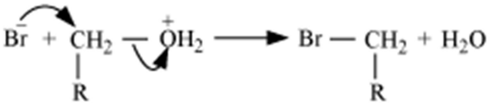
* Alcohols act both as nucleophiles and electrophiles.

* Alcohols as nucleophiles



* Protonated alcohols as electrophiles

$$R-CH_2-OH + H^+ \longrightarrow R-CH_2-\overset{+}{O}H_2$$

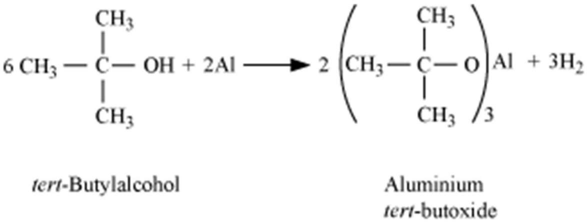


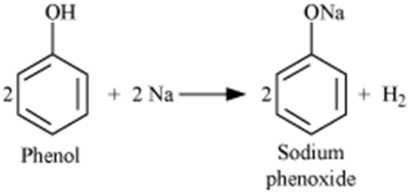
Reactions Involving Cleavage of O−H Bond

* **Acidity of alcohols and phenols**

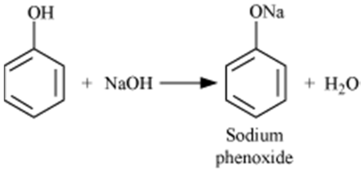
* Reaction with active metals such as Na, K and Al

$$2R-O-H+2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2R-O-Na} + H_2$$





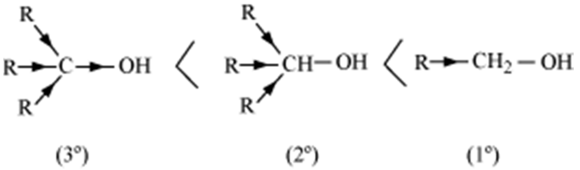
* Phenols react with aq. NaOH to form sodium phenoxides.



* Acidity of phenols

* Acidic character arises due to the polar nature of O− H

* The acid strength of alcohols increases in the order

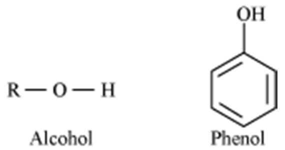


* Alcohols are weaker acids than water.

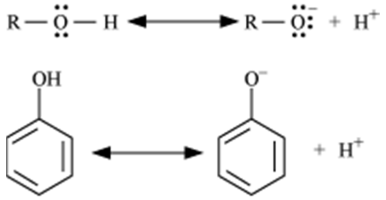
* Alcohols act as Bronsted bases as well.

* Phenols are stronger acids than alcohols.

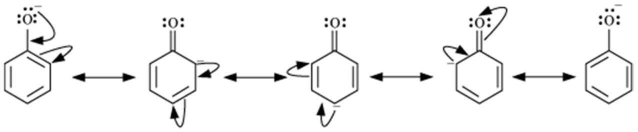
* Reason:



In alcohol, −OH is attached to the sp^3 hybridised carbon whereas in phenol, −OH is attached to the sp^2 hybridised carbon. Since sp^2 hybridised carbon is more electronegative than sp^3hybridised carbon, electron density on the oxygen atom in phenol decreases. As a result, the polarity of O−H bond increases, and hence, ionisation of phenol increases. This leads to increase in the acidity of phenols.



Phenoxide ion is more stable than alkoxide ion due its resonance stabilisation.



Therefore, phenol is more acidic than alcohol.

* Electron-withdrawing substituents (especially at *ortho-* and *para-* positions) increase the acidity of phenols whereas electron-donating substituents decrease acidity.

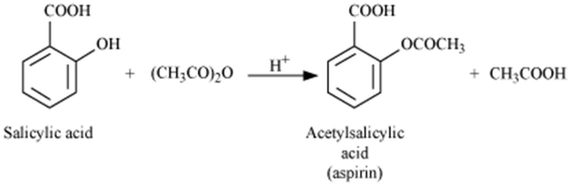
Esterification

* $$\text{Ar/R}-\text{OH} + \underset{\text{Carboxylic acid}}{\text{R}'-\text{COOH}} \overset{H^+}{\longleftrightarrow} \text{Ar/ROCOR}' + H_2O$$

* $$\text{Ar/R}-\text{OH} + \underset{\text{Acid anhydride}}{(\text{R}'\text{CO})_2\text{O}} \overset{H^+}{\longleftrightarrow} \text{Ar/ROCOR}' + \text{R}'\text{COOH}$$

* $$\text{Ar/R}-\text{OH} + \underset{\text{Acid Chloride}}{\text{R}'\text{COCl}} \overset{\text{Pyridine}}{\longleftrightarrow} \text{Ar/ROCOR}' + \text{HCl}$$

* Example − Acetylation of salicylic acid



Reactions Involving Cleavage of C−O Bond in Alcohols

Reaction with hydrogen halides:

$$R-OH + HX \xrightarrow{ZnCl_2} R-X + H_2O$$

* Lucas test [test with Lucas regent (conc. HCl and $ZnCl_2$)] − Used for distinguishing the three classes of alcohols.

Reaction with phosphorus trihalides:

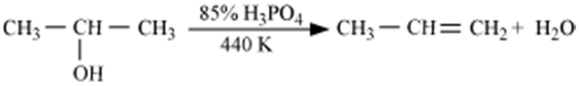
$$3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3 (X = Cl, Br)$$

Dehydration:

From 1° alcohol

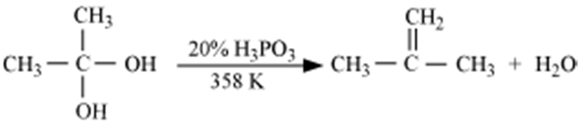
$$C_2H_5OH \xrightarrow[443\ K]{\text{Conc. } H_2SO_4} CH_2 = CH_2 + H_2O$$

From 2° alcohol



$$CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3 \xrightarrow[440\ K]{85\%\ H_3PO_4} CH_3 - CH = CH_2 + H_2O$$

From 3° alcohol

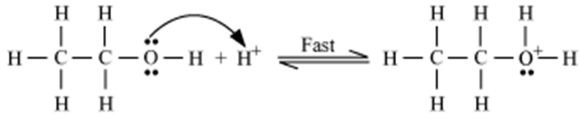


$$CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}} - OH \xrightarrow[358\ K]{20\%\ H_3PO_3} CH_3 - \overset{\overset{CH_2}{\|}}{C} - CH_3 + H_2O$$

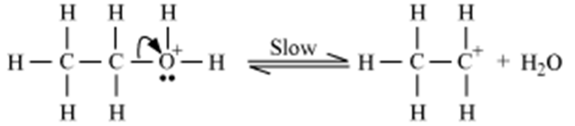
Therefore, the order reactivity can be observed as 1° < 2° < 3°

* Mechanism of dehydration

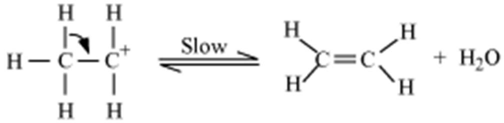
Step 1 − Formation of protonated alcohols



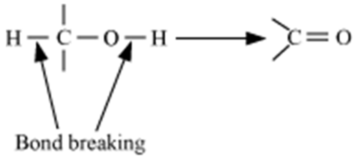
Step 2 − Formation of carbocation



Step 3 − Formation of alkene by elimination of a proton

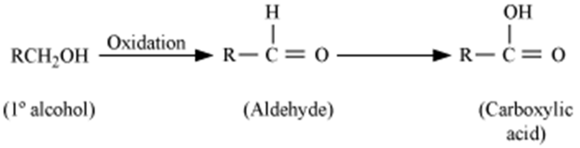


* **Oxidation:** Involves formation of a carbon− oxygen double bond, with cleavage of O− H and C− H bonds



* Also known as dehydrogenation as dihydrogen is lost.

* Depending on the oxidising agent, a primary alcohol is oxidised to aldehydes and then to carboxylic acid.



$$\underset{(1^\circ \text{ alcohol})}{RCH_2OH} \xrightarrow{\text{Oxidation}} \underset{(\text{Aldehyde})}{R-\overset{H}{\overset{|}{C}}=O} \longrightarrow \underset{(\text{Carboxylic acid})}{R-\overset{OH}{\overset{|}{C}}=O}$$

* Oxidising agents such as potassium dichromate converts primary alcohol to aldehydes and resist further oxidation.

* Strong oxidising agents such as acidified $KMnO_4$ convert alcohols directly into carboxylic acid.

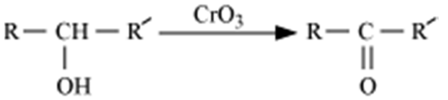
$$RCH_2OH \xrightarrow{\text{acidefied } KMnO_4} RCOOH$$

* Reagents such as CrO_3 in anhydrous medium, PCC (pyridinium chlorochromate) are used for isolation of aldehydes.

$$RCH_2OH \xrightarrow{CrO_3} RCHO$$

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

* 2° alcohols are converted into ketones by CrO_3

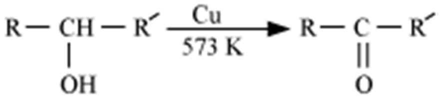


$$R-\underset{OH}{\underset{|}{CH}}-R' \xrightarrow{CrO_3} R-\underset{O}{\underset{||}{C}}-R'$$

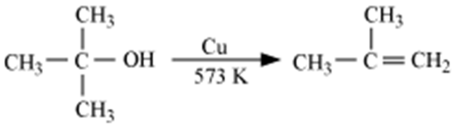
* 3° alcohols do not undergo oxidation; however, under strong oxidising agents such as $KMnO_4$ and high temperature, a mixture of carboxylic acids containing lesser number of carbon atoms is formed.

* Reaction with heated copper at 573 K

$$RCH_2OH \xrightarrow[573K]{Cu} RCHO$$



$$R-\underset{OH}{\underset{|}{CH}}-R' \xrightarrow[573\text{ K}]{Cu} R-\underset{O}{\underset{||}{C}}-R'$$



$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH \xrightarrow[573\text{ K}]{Cu} CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2$$

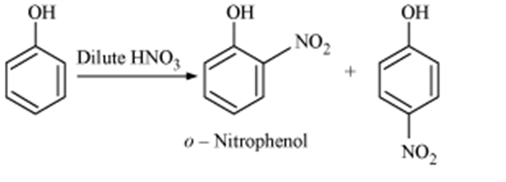
Reactions of Phenols

Electrophilic Aromatic Substitution

* The −OH group activates the benzene ring towards electrophilic substitution and directs the incoming group to *ortho*- and *para*-positions.

Nitration

* With dilute HNO_3

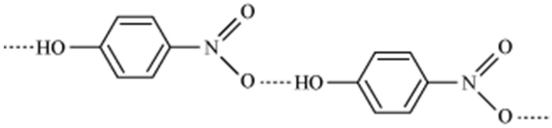


o – Nitrophenol

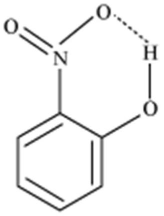
p – Nitrophenol

The *o*- and *p*-isomers can be separated by steam distillation.

Reason: *p*-nitrophenol is less volatile due to the association of molecules by intermolecular H-bonding, while *o*-nitrophenol is steam volatile due to intramolecular H-bonding.

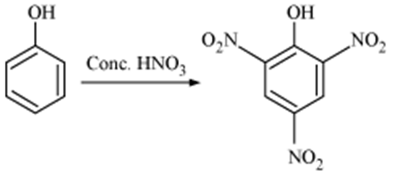


Intermolecular H–bonding in *p*–Nitrophenol



Intramolecular H–bonding in *o*–Nitrophenol

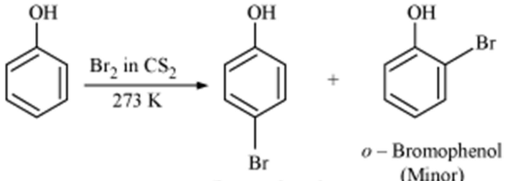
* With concentrated HNO_3:



2, 4, 6 – Trinitrophenol
(Picric acid)

Halogenation

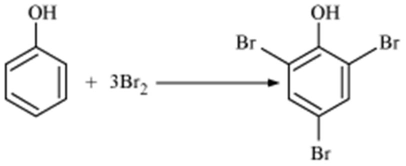
* Reaction carried out in solvents such as CS_2 or $CHCl_3$:



p – Bromophenol
(Major)

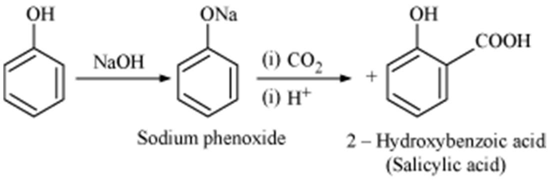
o – Bromophenol
(Minor)

* With bromine water:

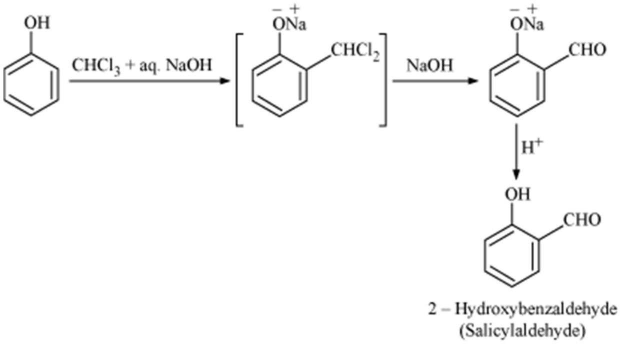


2, 4, 6 – Tribromophenol

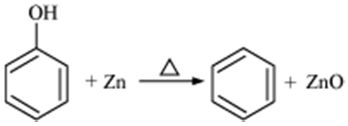
Kolbe's Reaction



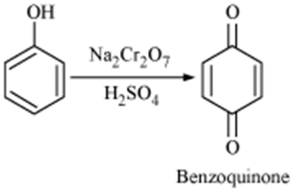
Reimer-Tiemann Reaction



Reaction with Zinc Dust



Oxidation



The presence of phenol can be confirmed by converting it to phenolphthalein which turns pink in basic solution.

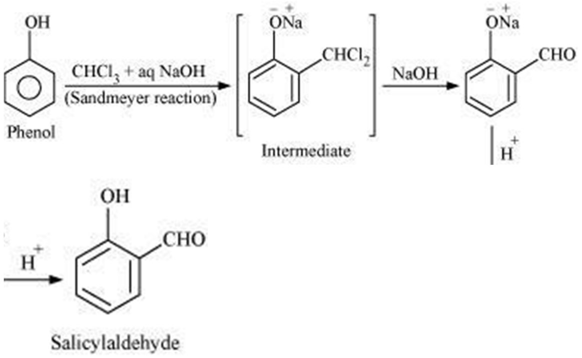
Solved Examples

Ex.8 Write the names of reagents and equations in the conversion of phenol to salicyl aldehyde

Or

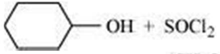
Give an illustration of Reimer−Teimann reaction.

Sol.

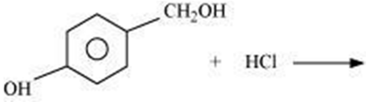


Ex.9 Complete the following reaction equations:

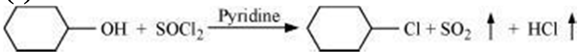
(i)



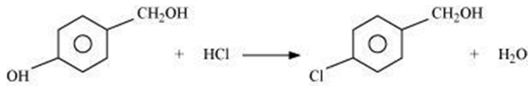
(ii)



Sol. (i)



(ii)



Some Commercially Important Alcohols

Methanol (CH_3OH)

- Known as wood spirit
- Preparation
- Earlier produced by destructive distillation of wood
- Catalytic hydrogenation of carbon monoxide

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

- Properties
- Colourless liquid
- Boiling point = 337 K
- Highly poisonous − Small quantities cause blindness and large quantities cause even death.
- Uses
- As a solvent in paints and varnishes
- In the preparation of formaldehyde (HCHO)

Ethanol (C_2H_5OH)

- Preparation
- By fermentation

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

- Molasses Glucose Fructose

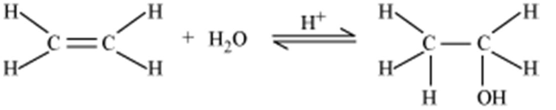
$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$

- Glucose/Fructose

When the percentage of alcohol formed exceeds 14%, the action of zymase is inhibited.

Fermentation takes place in absence of air. If air gets into fermentation mixture, then ethanol is oxidised to ethanoic acid by the oxygen present in air and as a result, the taste of alcoholic drink is destroyed.

- By hydration of ethane



- Properties
- Colourless liquid
- Boiling point = 351 K
- Uses
- As a solvent in manufacture of paint and a number of carbon compounds
- Denaturation of alcohol − Commercial alcohol becomes unfit for drinking by mixing some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). This is known as **denaturation** of alcohol.

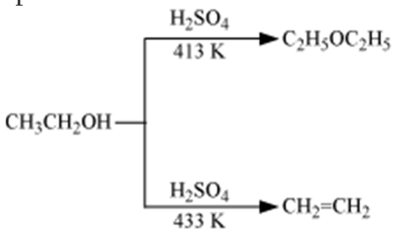
Ethers

Preparation

By dehydration of alcohols

- Alcohols undergo dehydration in the presence of protic acids like H_2SO_4, H_3PO_4.
- Product may be alkene or ether depending on the reaction conditions.

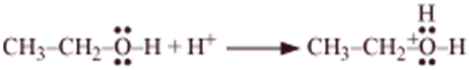
Example:



- Mechanism:

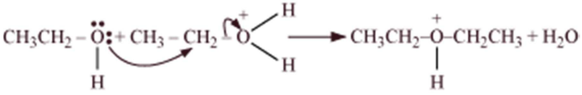
Formation of ether follows S_N2 mechanism.

Step 1



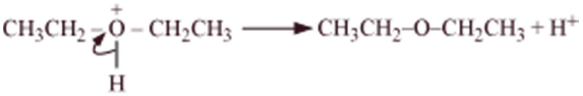
$CH_3-CH_2-\ddot{\underset{..}{O}}-H + H^+ \longrightarrow CH_3-CH_2-\overset{H}{\overset{|}{\overset{+}{O}}}-H$

Step 2



$CH_3CH_2-\ddot{O}: + CH_3-CH_2-\overset{+}{O}H_2 \longrightarrow CH_3CH_2-\overset{+}{O}(H)-CH_2CH_3 + H_2O$

Step 3



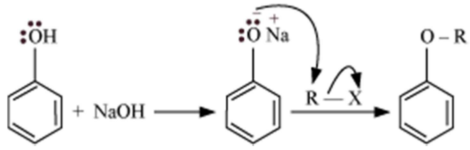
$CH_3CH_2-\overset{+}{O}(H)-CH_2CH_3 \longrightarrow CH_3CH_2-O-CH_2CH_3 + H^+$

- This method is applied to prepare ethers having primary alkyl groups only.
- When the alkyl group is 2° or 3°, elimination competes over substitution, and this leads to the formation of alkene.

Williamson synthesis

$R-X + R'-\ddot{\underset{..}{O}}\ Na \longrightarrow R-\ddot{\underset{..}{O}}-R' + NaX$

- Better results are obtained if the alkyl halide is 1°. For 2° and 3° halides, elimination competes over substitution to form alkenes.
- Reason:Alkoxides are nucleophiles as well as strong bases. They react with alkyl halides, leading to elimination reactions.
- This method can be used for converting phenols to ethers also.



Solved Examples

Ex.10 Write chemical reaction equations to illustrate the following reactions:
Williamson synthesis of ethers

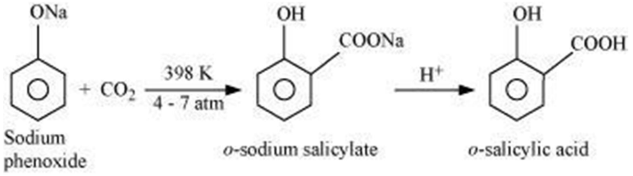
Sol. *Williamson synthesis of ethers*: It is used for preparing both symmetrical and unsymmetrical ethers. It involves the treatment of alkyl halide with sodium alkoxide or sodium phenoxide to give ether and a sodium salt of halide.

$$CH_3I + NaOC_2H_5 \longrightarrow CH_3OC_2H_5 + NaI$$

Ex.11 Illustrate the following reactions giving a chemical equation for each:

(i) Kolbe's reaction,
(ii) Williamson synthesis.

Sol. (i) **Kolbe's Reaction :** It involves the reaction between sodium phenoxide and carbon dioxide under a pressure of 4 − 7 atmospheres at 398 K to form sodium salicylate which on hydrolysis with minerals acids gives salicylic acid.



(ii) Williamson synthesis : This reaction is used to prepare both symmetrical as well as unsymmetrical ethers. It involves the treatment of alkyl halide with sodium alkoxide or sodium phenoxide.

CH_3I	+	$NaOC_2H_5$	$\longrightarrow$	$CH_3OC_2H_5$	+	NaI
Methyl iodide		Sodium ethoxide		Methoxy ethane		

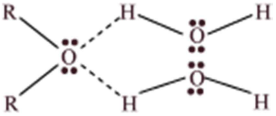
Physical Properties

Boiling point

- * Comparable to those of alkanes, but much lower than those of alcohols of comparable molecular mass
- * Reason: Alcohols undergo intermolecular H− bonding while ethers do not

Solubility

- * Soluble in water
- * Reason: Form H− bonds with water



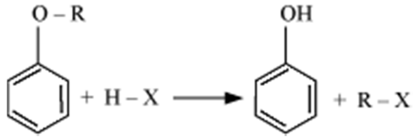
Chemical Reactions

- * Cleavage of C− O bond in ethers
- * React with excess of hydrogen halide under drastic conditions. Dialkyl ethers give two alkyl halide molecules.

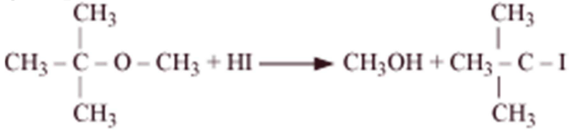
$$R-O-R+HX \longrightarrow RX+R-OH$$

$$R-OH+HX \longrightarrow R-X+H_2O$$

- * Alkyl aryl ethers react with hydrogen halide to give phenol and alkyl halide. Aryl− oxygen bond is not cleaved due to the high stability of aryl− oxygen bond.



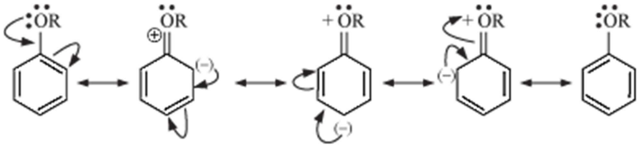
- * When the two alkyl groups are different, one alkyl halide molecule and one alcohol molecule is formed.
- * The order of reactivity of hydrogen halide is HCl < HBr < HI
- * When one of the alkyl groups is tertiary, the alkyl halide is formed from the tertiary alkyl group.



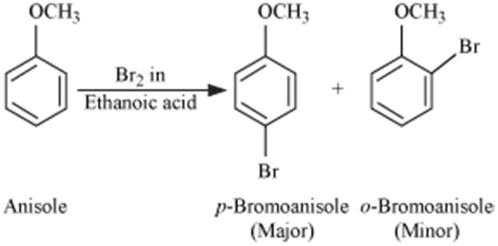
$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-O-CH_3+HI \longrightarrow CH_3OH+CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-I$$

Electrophilic substitution

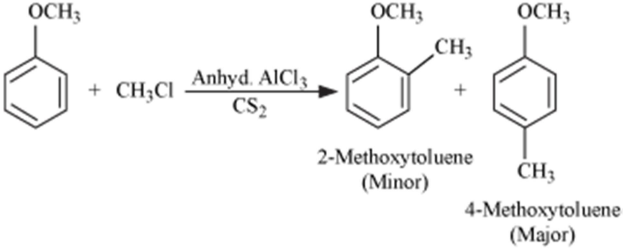
- * The alkoxy (− OR) group is *ortho*− and *para*− directing, and activates the aromatic ring towards electrophilic substitution due to resonance.



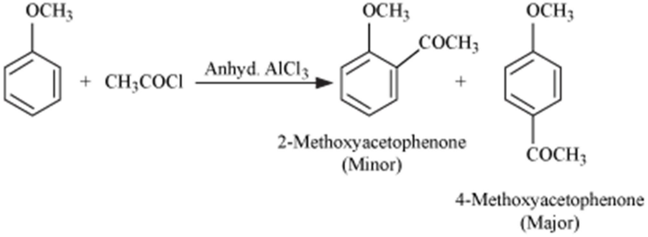
- * Halogenation



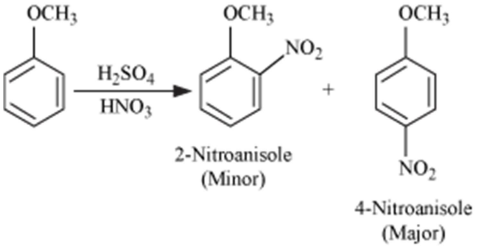
- * Friedel-Crafts alkylation



- * Friedel-Crafts Acylation



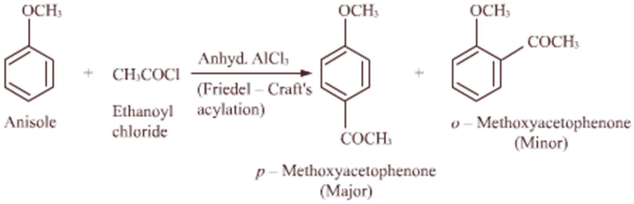
- * Nitration



Solved Examples

Ex.12 Write the names of reagents and equations in the conversion of anisole to *p*-methoxyacetophenone

Sol.



Ex.13 How are formalin and trioxane related to methanal?

Sol. Formalin is a saturated solution of methanal in water (about 40% or 37% by mass).

Trioxane ($C_3H_6O_3$) is a cyclic trimer of methanal.

Trioxane