INTRODUCTION

(a) These are the organic compounds in which –OH group is directly attached with carbon.
(b) These are hydroxy derivatives of alkanes and mono alkyl derivatives of water.
(c) Their general formula is C\textsubscript{n}H\textsubscript{2n+1}OH or C\textsubscript{n}H\textsubscript{2n+2}O.
(d) The hybridisation state of carbon is sp\textsuperscript{3}.
(e) Geometry is tetrahedral.
(f) In these compounds C-O bond length is 1.42 Å.
(g) These are of following types, depending upon the no. of OH groups.
(i) Monohydric alcohol : Contains one –OH group only, eg.C\textsubscript{2}H\textsubscript{5}OH
(ii) Dihydric alcohol : Contains two –OH groups. eg. glycol
(iii) Trihydric alcohol : Contains three –OH groups eg. glycerol
(iv) Polyhydric alcohol : Contains more than three - OH groups. eg. sorbitol, manitol.
(h) Alcohol shows chain, position & functional group isomerism. If chiral carbon atom is present, they shows optical isomerism.

METHODS OF PREPARATION

From Alkyl halides :
Alkyl halides reacts with aq. KOH/aq. AgOH or H\textsubscript{2}O and forms alcohol.
\[
\begin{align*}
R-\text{CH}_2-X + K-OH (aq.) & \rightarrow R-\text{CH}_2OH + KX \\
R-\text{CH}-X + AgOH (aq.) & \rightarrow R-\text{CH}-OH + AgX \\
R-C-X + H-OH & \rightarrow R-C-OH + HX
\end{align*}
\]

From Alkenes :
Hydration – Alkenes are catalytically hydrated by dilute mineral acid solution.
\[
\begin{align*}
\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} & \xrightarrow{\text{aq.} \text{H}_2\text{SO}_4} \text{CH}_3\text{CH}_2\text{OH} \\
R-\text{CH} = \text{CH}_2 + \text{H}_2\text{O} & \xrightarrow{\text{aq.} \text{H}_2\text{SO}_4} R-\text{CH} - \text{CH}_3
\end{align*}
\]

Oxymercuration -- demercuration :
Alkenes react with mercuric acetate in the presence of water to give hydroxymercurial compounds, which on reduction yield alcohols. (Markovnikov addition)
\[
\begin{align*}
>\text{C} = \text{C}< + \text{H}_2\text{O} + \text{Hg} (\text{OAc})_2 & \rightarrow \text{C} - \text{C} - \xrightarrow{\text{NaBH}_4} \text{C} - \text{C} - \\
\text{OH Hg O Ac} & \text{OH H}
\end{align*}
\]
Mercuric acetate Alcohol
Hydroboration – Oxidation:
(Anti-Markownikov orientation)

\[ >C = C< + \frac{1}{2} (BH_3)_2 \rightarrow B\left(\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C}< \\
\text{H}
\end{array}\right) \]

Alkene  Diborane  Tri alkyl borane

\[
\frac{H_2O}{OH} \rightarrow \frac{H}{OH} + \text{B(OH)}_3
\]

By Reduction of Carbonyl compounds:

\[
R-C-H + 2H \xrightarrow{\text{LiAlH}_4/\text{Na} + \text{C}_2\text{H}_5\text{OH}} R-\text{CH}_2\text{OH}
\]

1° alcohol

\[
R-C-R + 2H \xrightarrow{\text{LiAlH}_4/\text{Na} + \text{C}_2\text{H}_5\text{OH}} R-\text{CH-R}
\]

2° alcohol

Note:
(i) We cannot obtain 3° alcohol from this method
(ii) If we use NaH as reductant then the process is called as 'Darzen's process'.

By Reduction of Acid & its derivatives:

\[
R-C-OH + 4H \xrightarrow{\text{LiAlH}_4} R\text{CH}_2\text{OH}
\]

\[
R-C-X + 4H \xrightarrow{\text{LiAlH}_4} R\text{CH}_2\text{OH} + \text{HX}
\]

\[
R-C-\text{OR}' + 4H \xrightarrow{\text{LiAlH}_4} R\text{CH}_2\text{OH} + R'\text{OH}
\]

\[
\text{RCOOCOR} + 8H \xrightarrow{\text{LiAlH}_4} 2 R\text{CH}_2\text{OH} + \text{H}_2\text{O}
\]

Important Note: Acid amide does not form alcohol on reduction. It forms primary amine.

From Grignard reagent:
With oxygen: –
Grignard reagent forms alcohol of same no. of carbon atoms as in Grignard reagent.

\[
2R-\text{Mg-X} + O_2 \xrightarrow{\Delta/\text{Al}_2\text{O}_3} 2R-\text{O-Mg-X} \xrightarrow{\text{ZnOH}} 2\text{ROH} + 2 \text{Mg(X)OH}
\]

With ethylene oxide:

\[
\text{R}^\delta(+\text{Mg}^+\text{X}) + \overset{\delta^+}{\overset{\delta^-}{\text{CH}_2-\text{CH}_2}} \rightarrow \text{R-CH}_2-\text{CH}_2\text{O-Mg-X} \xrightarrow{\text{H}_2\text{O}} \text{R-CH}_2-\text{CH}_2\text{OH} + \text{Mg(X)OH}
\]

[Alcohol with two carbon more than Grignard reagent]
With carbonyl compounds: $\mathrm{R}^\delta - \mathrm{Mg}^- - \mathrm{X}^+ + \mathrm{R'}^\delta - \mathrm{C}^- - \mathrm{H} \rightarrow \mathrm{R}^\delta - \mathrm{C}^- - \mathrm{R}' \xrightarrow{\text{H}_2\text{O}} \mathrm{R}^\delta - \mathrm{C}^- - \mathrm{R'}^\delta - \mathrm{O}^\delta - \mathrm{Mg}^- - \mathrm{X}^+ - \mathrm{OH}^{-}

Note:
(i) If $\mathrm{R}' = \mathrm{H}$, Product will be 1° alcohol.
(ii) If $\mathrm{R}' = \mathrm{R}$, Product will be 2° alcohol.
(iii) If carbonyl compound is ketone, product will be 3° alcohol.
(iv) It is the best method for preparation of alcohol because we can prepare every type of alcohols.

From Primary amines: -

$\mathrm{R}^-\mathrm{NH}_2 + \mathrm{HNO}_2 \xrightarrow{\text{H}_2\text{O}} \mathrm{R}^-\mathrm{OH} + \mathrm{N}_2 + \mathrm{H}_2\mathrm{O}$.

But it is not a good method for preparation of alcohol because a number of byproducts are formed in this reaction like alkyl chloride, alkyl nitrite, alkene and ether.

Note: In this reaction if we take ethyl amine then main product will be ethanol while if we take methyl amine, then main product will be dimethyl ether.

**PHYSICAL PROPERTIES**

(a) Alcohols are colourless with specific smell liquid. They are soluble in water due to H-bonding. These are partially soluble in organic solvents.
(b) They are liquid in nature up to 12-carbon.
(c) Melting point and Boiling point $\propto \frac{1}{\text{molecular mass} \times \text{No. of branches}}$
(d) Boiling point of alcohols are higher than equivalent ethers. It is due to H-bonding.
(e) Alcohols are poisonous in nature also. Poisonous character increase with increment in molecular weight or branching. Ethanol is exception, which is non-poisonous in nature. It is most useful organic solvent.
(f) Methanol causes blindness.
(g) Isopropyl alcohol is called as rubbing alcohol.
(h) Cholesterol is also an example of complex alcohol which is called notorious alcohol because it causes heart attack.
(i) Viscous nature of alcohol is directly proportional to H-bonding or number of -OH groups. That is why we can say alcohol is less viscous than glycerol & manitol is more viscous than glycerol.
(j) Ethanol is liquid while glucose is solid. It is due to more H-bonding in glucose.

**CHEMICAL PROPERTIES**

Chemical reactions of alcohols are classified in the following three types:-
(i) Reaction of H atom of -OH group of Alcohols
(ii) Reaction of OH group of Alcohols
(iii) General reaction of Alcohols.
Reaction of H atom of –OH group of Alcohols:
These are the reactions in which alcohol shows acidic character.

Reaction with Na:
\[2R-O-H + Na \rightarrow 2R - O - Na + H_2↑\]
The acidic order of alcohols is
MeOH > 1° > 2° > 3°

Esterification / Reaction with carboxylic acid:-
\[R-O-H + H-O-C-R \xrightarrow{\text{conc. } H_2SO_4} R-C-O-R + H_2O\]
ester

Mechanism:
\[H_2SO_4 \rightarrow H^+ + HSO_4^-\]
\[R-C-O-H + H^+ \rightarrow R-C-OH - H_2O \rightarrow R-C' \xrightarrow{ROH} R-O-C-R \xrightarrow{H^+} R-C-OR\]

Note: The above reaction is laboratory method of ester preparation.

Reaction with Acid derivatives:
\[R-O-H + X-C-R \xrightarrow{\text{conc. } H_2SO_4} R-O-C-R + HX\]

Reaction with Ketene:
\[
\begin{align*}
R-O-H + \text{CH}_2 = \text{C}^+ &= \text{CH}_3 - C-O-R \\
\text{O}^+ &
\end{align*}
\]

Reaction with Isocyanic Acid:
\[
\begin{align*}
\text{R-O-H} + \text{H-N}^+ &= \text{H-N} - \text{C-O-R} \rightarrow \text{H-NH-C-O-R} \\
&\text{amino ester (urethane)}
\end{align*}
\]

Reaction with ethylene oxide:
\[
\begin{align*}
\text{R-O^\delta^-} + \text{H^\delta+} + \text{CH}_2\text{CH}_2 &\rightarrow \text{CH}_2\text{CH}_2 \xrightarrow{\text{ROH}} \text{CH}_2\text{CH}_2 \\
&\text{1,2-dialkoxy ethane}
\end{align*}
\]

Reaction with Diazomethane:
\[R-O-H + CH_2N_2 \rightarrow R-O-CH_3\]
(ether)
Reaction of – OH group of Alcohols :-

Reaction with dry HX (Grove’s Process):
R–OH + HX $\rightarrow$ R – X + H₂O

Reaction with PCl₅:
R–OH + PCl₅ $\rightarrow$ R–Cl + POCI₃ + HCl

Reaction with PCl₃:
$3R$–OH + PCl₃ $\rightarrow 3R$–Cl + H₃PO₃

Reaction with SOCl₂ (Darzen reaction):
R–OH + SOCl₂ $\xrightarrow{\text{Pyridine}}$ R–Cl + SO₂ + HCl

Reaction with ammonia:
R – OH + NH₃ $\xrightarrow{\text{EtOH}, 20^\circ C}$ RNH₂ + H₂O

Reaction with HNO₃:
R–OH + HNO₃ $\rightarrow$ R–ON$\text{O}_\text{O}$ + H₂O
(conc.) alkyl nitrate (soluble ester)

**Mechanism :-**

\[ \text{HNO}_3 \rightarrow H^+ + \text{NO}_3^- \]

\[ \text{R–OH} + H^+ \xrightarrow{\text{aq}} \text{R} \o \text{O–H} \xrightarrow{\text{aq}} \text{R} \o \]

\[ \text{R} \o + \text{NO}_3^- \xrightarrow{\text{aq}} \text{R} \o \text{N} \o \]

alkyl nitrate

Reaction with H₂SO₄ :-

(i) \( C_2H_5OH + H\o \text{SO}_\text{OH} \xrightarrow{20-35^\circ \text{C}, \text{room temp}} C_2H_5\o \text{SO}_\text{OH} \)

stable upto (80-100°C)

(ii) \( \text{CH}_3\text{–CH}_2\text{–OH} + \text{H}_2\text{SO}_4 \xrightarrow{140^\circ \text{C}} \text{CH}_3\text{–CH}_2\text{–O–CH}_2\text{–CH}_3 \)

(excess)
Mechanism:

\[ H_2SO_4 \rightarrow H^+ + HSO_4^- \]

\[ CH_3-CH_2-\overset{\ominus}{\overset{\circ}{O}}-H + H^+ \rightarrow CH_3-CH_2-\overset{\circ}{O}^- + H_2O \]

\[ CH_3-CH_2-O-CH_2-CH_3 \leftarrow CH_3-CH_2-OH \quad \text{(protonated ether)} \]

\[ \quad \downarrow \ H^+ \]

\[ CH_3-CH_2-O-CH_2-CH_3 \quad \text{(excess)} \]

(iv) \[ CH_3-CH_2-OH + H_2SO_4 \rightarrow CH_2=CH_2 \]

Mechanism:

\[ H_2SO_4 \rightarrow H^+ + HSO_4^- \]

\[ CH_3-CH_2-\overset{\ominus}{\overset{\circ}{O}}-H + H^+ \rightarrow CH_3-CH_2-\overset{\circ}{O}^- + H_2O \rightarrow CH_3-CH_2-\overset{\ominus}{\overset{\circ}{O}}-H \rightarrow CH_2=CH_2 \]

Note: In the above reaction, excess of ethanol is present so, intermediate carbocation satisfies itself by elimination.

**GENERAL REACTION OF ALCOHOLS**

Reduction:

\[ R-OH + 2 HI \xrightarrow{\text{Heat}} R-H \]

Reacting species of solution is HCrO$_4$.$^-$.

\[ \begin{array}{c}
R-OH + [\text{acidic } \text{KMnO}_4] \\
\xrightarrow{\text{IO}} R-C=O + \text{H}_2O
\end{array} \]

\[ \begin{array}{c}
R-C-OH + [\text{acidic } \text{K}_2\text{Cr}_2\text{O}_7] \\
\xrightarrow{\text{IO}} R-C=O + \text{CO}_2 + \text{H}_2O + R-C-OH
\end{array} \]
Catalytic Oxidation / Dehydrogenation:

\[
\text{R-C-O} \xrightarrow{\text{Cu/ZnO}} \text{R-C}=\text{O}.
\]

1° alcohol \hspace{1cm} \text{aldehyde}

\[
\text{R-C-O} \xrightarrow{\text{Cu/ZnO}} \text{R-C-R}.
\]

secondary alcohol \hspace{1cm} \text{ketone}

\[
\text{R-C-OH} \xrightarrow{\text{Cu/ZnO}} \text{R-C-R}.
\]

tert. alcohol \hspace{1cm} \text{alkene}

(Note: This is dehydration process.)

Oxidation through Fenton’s Reagent:
Higher and branched alcohols are converted into diols through Fenton’s reagent. \((\text{FeSO}_4 + \text{H}_2\text{O}_2)\) is Fenton’s reagent.
\[
\text{Fe}^{+2} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{+3} + \cdot\text{OH} + \cdot\text{H}.
\]

\[
\text{CH}_3\text{C-CH}_2\text{-H} + \cdot\text{OH} \rightarrow \text{CH}_3\text{C-CH}_2\text{OH} + \text{H}_2\text{O}.
\]

\[
\text{CH}_3\text{C-CH}_2\text{CH}_3 + \text{CH}_3\text{C-CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{C-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3.
\]

\[
\text{2,5-dimethyl hexanediol-2,5}
\]

Self Condensation:
When alcohol is heated with sodium ethoxide then by self condensation they convert into higher alcohol.

\[
\text{RCH}_2\text{-CH}_2\text{-OH} + \text{H-CH-CH}_2\text{-OH} \rightarrow \text{RCH}_2\text{-CH}_2\text{-CH-CH}_2\text{-OH}.
\]

(higher alcohol)

Note: The above reaction is called as ‘Guerbet’s Reaction’.

Preparation of methanol:
Methanol is also called as carbinol or wood spirit.
From Water Gas:
\[
[\text{CO + H}_2] + \text{H}_2 \xrightarrow{\text{Cu/ZnO}} \text{CH}_3\text{OH}\ (90\%)
\]
From Methane :

\[ \text{CH}_4 + \frac{1}{2} \text{O}_2 \xrightarrow{\text{Cu tube} \atop 200^\circ\text{C}} \text{CH}_3\text{OH} \ (90\%) \]

Preparation of Ethanol :

From Ethene :

By hydration with dil. H\text{2SO}_4

\[ \text{CH}_2=\text{CH}_2 + \text{H} \cdot \text{OH} \xrightarrow{\text{dil. H}_2\text{SO}_4} \text{CH}_3 \cdot \text{CH}_2 \cdot \text{OH} \]

Preparation of ethanol from sugar :

(i) **Molasses** - Waste product in sugar industry is called molasses. It is a mixture of sugar (30%) and invert sugar (32-40%).

(ii) **Invert sugar** - Combine form of glucose and fructose is called as invert sugar.

\[ \text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{yeast cell}} \text{C}_{6}\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6 \]

<table>
<thead>
<tr>
<th></th>
<th>glucose</th>
<th>fructose</th>
</tr>
</thead>
</table>

\[ \text{C}_6\text{H}_{12}\text{O}_6 \xrightarrow{\text{yeast cell}} \text{C}_2\text{H}_5\text{OH} + \text{CO}_2 + \text{H}_2\text{O} \]

Note: Glucose and fructose are functional isomers.

Preparation of ethanol from starch :

(i) Starch solution is technically called 'Mesh'

(ii) Crushed germinated barley solution is called 'Malt'.

\[ 2\text{(C}_6\text{H}_{10}\text{O}_5)_n + n\text{H}_2\text{O} \xrightarrow{\text{maltase}} \text{nC}_{12}\text{H}_{22}\text{O}_{11} \]

<table>
<thead>
<tr>
<th>starch</th>
<th>maltose (wort)</th>
</tr>
</thead>
</table>

\[ \text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{maltase}} 2\text{C}_6\text{H}_{12}\text{O}_6 \]

<table>
<thead>
<tr>
<th>maltose</th>
<th>glucose</th>
</tr>
</thead>
</table>

\[ 2\text{C}_6\text{H}_{12}\text{O}_6 \xrightarrow{\text{zymase}} \text{C}_2\text{H}_5\text{OH} + \text{CO}_2 + \text{H}_2\text{O} + \text{energy} \]

(iii) From both of the methods conc. of ethanol achieved is 10-12% which is called 'Wash'.

(iv) Distillation of wash is done in special apparatus 'Coffee's still', which is based on counter current method. From this distillation yield of alcohol is 90%, which is called Raw spirit.

Raw spirit \[ \xrightarrow{\text{Fractional distillation}} 95.5\% \text{C}_2\text{H}_5\text{OH} + 4.5\% \text{H}_2\text{O} \]

(rectified spirit)

(v) Further purification is done in the following ways :

\[ 95.5\% \text{C}_2\text{H}_5\text{OH} + 4.5\% \text{H}_2\text{O} \xrightarrow{\text{Fractional distillation}} \text{C}_6\text{H}_6 + \text{H}_2\text{O} + \text{C}_2\text{H}_5\text{OH} + \text{Remaining C}_6\text{H}_6 \]

<table>
<thead>
<tr>
<th>(64°C)</th>
<th>(78.5 °C)</th>
<th>CH\text{3CHO}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(99.7%)</td>
<td>(68°C)</td>
<td></td>
</tr>
</tbody>
</table>
\[ C_2H_5OH + \text{Ca metal} \xrightarrow{2-3 \text{days}} C_2H_5OH + \text{Ca(OH)}_2 \]
(99.7%) (100%)
\[ C_2H_5OH + \text{anhy. CuSO}_4 \rightarrow C_2H_5OH + \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \]
(99.7%) white (100%)

**DIFFERENCE BETWEEN PRIMARY, SECONDARY & TERTIARY ALCOHOLS**

By **Oxidation Reaction**: Primary alcohol gives aldehyde on oxidation, secondary alcohol gives ketone and tertiary alcohols are resistant to oxidation.

By **Catalytic Oxidation / Dehydrogenation**: Primary alcohol gives aldehyde on oxidation, secondary alcohol gives ketone and tertiary alcohol gives alkene (dehydration takes place in this condition to tertiary alcohols.)

**Lucas Test**: A mixture of (anhydrous ZnCl\(_2\) + Conc. H\(_2\)SO\(_4\)) is called as Lucas Reagent.
(i) 3\(^\circ\) alcohol gives white ppt. with lucas reagent in 2-3 seconds only.
(ii) 2\(^\circ\) alcohol takes 9 - 10 minutes.
(iii) 1\(^\circ\) alcohol does not gives white ppt. at room temperature.

**Victor Meyer Test** :-
This test is also known as RBW (Red, Blue, White) test.

(a) \[ R-\text{CH}_2-\text{OH} \xrightarrow{\text{Red P/I}_2} R-\text{CH}_2-\text{I} \xrightarrow{\text{AgNO}_3/\text{AgI}} R-\text{CH}_2-\text{NO}_2 + \text{HNO}_2 \]
nitrate

![Nitric acid structure](image)

(b) \[ R_2-\text{CH-} \xrightarrow{\text{Red P/I}_2} R_2-\text{CH-I} \xrightarrow{\text{AgNO}_3} R_2-\text{CH-NO}_2 + \text{NO}_2 \]
No reaction
Pseudonitrole
(Blue colour)

(c) \[ R_3-\text{C-} \xrightarrow{\text{Red P/I}_2} R_3-\text{C-I} \xrightarrow{\text{AgNO}_3} R_3-\text{C-NO}_2 \xrightarrow{\text{HNO}_2} \text{no. reaction.} \]
Difference between Methanol and Ethanol

<table>
<thead>
<tr>
<th>Methanol</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. When CH₃OH is heated on Cu coil it gives formalin like smell.</td>
<td>Ethanol does not give formalin like smell.</td>
</tr>
<tr>
<td>2. When CH₃OH is heated with salicylic acid in H₂SO₄ (conc.) then methyl salicylate is formed which has odour like winter green oil</td>
<td>No such odour is given by ethanol</td>
</tr>
<tr>
<td>3. It does not give haloform or iodoform test.</td>
<td>It gives haloform test.</td>
</tr>
</tbody>
</table>

**MCQ**

**Q.1** Which of the following reaction is called 'Bouveault-Blanc reduction' -
(A) Reduction of acyl halide through Na/C₂H₅OH
(B) Reduction of ester through Na/C₂H₅OH
(C) Reduction of anhydride through Na/C₂H₅OH
(D) Reduction of carbonyl compounds through Na/C₂H₅OH

**Q.2** In which of the following reaction alcohol is not formed -
(A) \( R - \text{CH} = \text{CH}_2 + \text{H}_2 \xrightarrow{\text{NaOH}} \text{RCH}_2\text{CH}_3 \)
(B) \( R - \text{COCl} + 2\text{H}_2 \xrightarrow{\text{HCl}} \text{RCH}_2\text{CH}_3 \)
(C) \( (R - \text{CO})\text{O} + 4\text{H}_2 \xrightarrow{\text{Lithium}} \text{RCH}_2\text{CH}_3 \)
(D) \( R - \text{CH}_2 - \text{CH}_3 + \text{H}_2\text{O} \xrightarrow{\text{NaOH}} \)

**Q.3** Which one of the following alcohol has highest boiling point -
(A) Methanol  (B) Ethanol  (C) Propanol  (D) Isopropanol

**Q.4** Dimethyl ether and ethanol have same molecular weight but boiling point of ethanol is greater than dimethyl ether, cause of this is that dimethyl ether -
(A) Having less no. of branches
(B) Arrangement of hydrogen is different
(C) Due to hydrogen bonding in alcohol
(D) None of these

**Q.5** Reactivity order of alcohols towards Na will be -
(A) \( 3^\circ > 2^\circ > 1^\circ > \text{MeOH} \)  (B) \( \text{MeOH} > 1^\circ > 2^\circ > 3^\circ \)
(C) \( 2^\circ > 1^\circ > 3^\circ > \text{MeOH} \)  (D) \( 1^\circ = 2^\circ = 3^\circ = \text{MeOH} \)

**Q.6** In the esterification of alcohol by carboxylic acid, proton is given by -
(A) Alcohol  (B) Conc. H₂SO₄  (C) Acid carboxylic  (D) None of these
Q.7  2-methyl 2-propanol with Fenton's reagent gives -
(A) 1,2-methyl propene -1  (B) 2-methyl propene -2
(C) 2,5-dimethyl hexanediol-2,5  (D) 2,2,3,3 - tetramethyl butane

Q.8  When methane is passed in copper tube at 200°C with air, it gives -
(A) Methanol  (B) Ethanol  (C) Acetylene  (D) Ethene

Q.9  Acetic acid is removed from pyroligneous acid by the passing it in -
(A) Al (OH)₃ solution  (B) Ba (OH)₂ solution
(C) Ca (OH)₂ solution  (D) Ethanol

Q.10 Crushed germinated barley solution is called-
(A) Mesh  (B) Malt  (C) Wort  (D) Wash

Q.11 Which one test is also known as RBW test-
(A) Lucas test  (B) Victor Meyer test
(C) Carbilamine test  (D) Mullican-Barker test

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ANSWER KEY

<table>
<thead>
<tr>
<th>Q.1</th>
<th>Q.2</th>
<th>Q.3</th>
<th>Q.4</th>
<th>Q.5</th>
<th>Q.6</th>
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<td>(D)</td>
<td>(D)</td>
<td>(C)</td>
<td>(C)</td>
<td>(B)</td>
<td>(B)</td>
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<tr>
<td>(C)</td>
<td>(A)</td>
<td>(C)</td>
<td>(Q.10)</td>
<td>(B)</td>
<td>(Q.11)</td>
</tr>
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</table>
Formation of EtOH by fermentation -

1. Cane sugar → Crystallization
   → Molasses
   → Invertase (hydrolysis)
   → Invert sugar
   → Zymase (Fermentation)
   → EtOH

2. Grain → Starch → Diastase → Maltose
   → Maltase (Hydrolysis)
   → Glucose
   → Zymase (Fermentation)
   → EtOH
ETHERS

INTRODUCTION

(a) It is dialkyl derivative of water or alkoxy derivative of alkane or monoalkyl derivative of alcohols.
(b) Their general formula is \( C_nH_{2n+2}O \) or \( C_nH_{2n+1}O \)
(c) Hybridisation state of oxygen is \( sp^3 \) and bond angle is 110° due to counter balance repulsion of alkyl groups.
(d) If both alkyl groups are similar then these are called as simple ether, if different they are called as mixed ether.
(e) Carbon oxygen bond length is 1.42 Å.
(f) Ether shows chain, position metamerism and functional isomerism. Ethers are functional isomers of alcohols.
(g) In IUPAC system ethers are called as ‘Alkoxyl alkane’.
(h) Ethers are compounds of the general formula \( R — O — R, Ar — O — R \) or \( Ar — O — Ar \), where \( Ar \) is an aromatic group.
(i) An ether is symmetrical if the two groups attached to the oxygen atom are the same, and it is unsymmetrical if the groups are different.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 & \quad \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3 \\
\text{OCH}_3 & \quad \text{1-Ethoxypropane} \\
\text{3-Methoxyhexane} &
\end{align*}
\]

PREPARATION

1. Dehydration of alcohols

\[
2R — O — H \xrightarrow{\Delta} R — O — R + H_2O
\]

A water molecule is lost for every pair of alcohol molecules. Dehydration is limited to the preparation of symmetrical ethers, because a combination of two different alcohols yields a mixture of three ethers.

Alcohols can also dehydrate to alkenes, but dehydration to ethers is controlled by the choice of reaction conditions.

Example:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} & \xrightarrow{\text{H}_2\text{SO}_4 \text{ Conc.}} \xrightarrow{140^\circ\text{C}} \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \quad \text{Diethyl ether} \\
\text{CH}_3\text{CH}_2\text{OH} & \xrightarrow{\text{H}_2\text{SO}_4} \xrightarrow{180^\circ\text{C}} \text{CH}_=\text{CH}_2 \quad \text{Ethene}
\end{align*}
\]

Ether formation by dehydration is an example of nucleophilic substitution: protonated alcohol is the substrate and the second molecule of alcohol is the nucleophile.

The reaction is \( S_N^1 \) for \( 2^\circ \) and \( 3^\circ \) alcohols and \( S_N^2 \) for \( 1^\circ \) alcohol.
2. **Williamson synthesis**

\[
\begin{align*}
&\text{RX} \quad \text{R'OH} \quad \text{ArO Na}^- \\
\xrightarrow{\text{Na}} &\text{R'OR'} \quad \text{R - OAr}
\end{align*}
\]

Yield from RX: CH\(_3\) > 1° > 2° > 3°

The reaction involves the nucleophilic substitution of an alkoxide (or phenoxide) ion for a halide ion. This method can be used for preparing symmetrical as well as asymmetrical ethers.

\[(\text{CH}_3)_2\text{CH(OH)} \xrightarrow{\text{Na}} (\text{CH}_3)_2\text{CHO}^-\text{Na}^+ + \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \rightarrow \text{CH}_3(\text{CH}_3)_2\text{O} \text{CH(CH}_3)_2\]

\[
\text{OHH} + \text{CH}_3\text{CH}_2\text{Br} \xrightarrow{\text{aq. NaOH}} \text{OHH} \text{CH}_3\text{CH}_2\text{Br}
\]

Ethoxybenzene

The reaction gives the best yield with 1° alkyl halides. With tertiary alkyl halides, elimination becomes an important reaction and no ether is obtained.

\[
\begin{align*}
\text{CH}_3 & - \text{C} - \text{Br} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{aq. NaOH}} \text{CH}_3 - \text{C} = \text{CH}_2
\end{align*}
\]

**PHYSICAL PROPERTIES**

1. The C — O — C bond angle in ethers is not 180° and the dipole moments of the two C — O bonds do not cancel each other. Hence, ethers possess a small net dipole moment.

\[
\begin{align*}
\text{R} & \quad \text{net dipole moment} \\
\xrightarrow{110^\circ} & \text{O}
\end{align*}
\]

2. The boiling point of ethers are the same as those of alkanes of comparable molecular weights. The boiling points of alcohols are much higher than those of ethers, as ethers are incapable for intermolecular hydrogen bonding.

3. The solubility of ethers in water is comparable to that of alcohols, because ethers can form hydrogen bonds with water molecules.
CHEMICAL PROPERTIES

Ethers are unreactive compounds. The ether linkage is quite stable towards bases, oxidising, and reducing agents.

1. **Cleavage by acids**

\[
R - O - R' + HX \rightarrow R - X + R'OH
\]

Reactivity of HX: HI > HBr > HCl.

Cleavage takes place under vigorous conditions using concentrated acids and high temperature. A dialkyl ether initially yields an alkyl halide and an alcohol; the alcohol may further react to form second mole of alkyl halide.

\[
\begin{align*}
\text{CH}_3 & - \text{CH} - \text{O} - \text{CH} & - \text{CH}_3 \\
& & \text{CH}_3
\end{align*}
\]

130 - 140°C \[\text{Br}
\]

48% HBr \[\rightarrow \]

2CH₃CH₂CH₃

The initial reaction between an ether and an acid results in the formation of a protonated ether. The cleavage then involves a nucleophilic attack by a halide ion on this protonated ether with the displacement of the weakly basic alcohol molecule.

\[
R - O - R' + HX \rightarrow R - O - R' + X \xrightarrow{\text{S}_\text{N}1\text{ or S}_\text{N}2} R - X + R'OH \quad \text{HX} \rightarrow R'X
\]

Protonated ether

A primary alkyl group tends to undergo Sₙ₂ displacement and a tertiary alkyl group tends to undergo Sₙ₁ displacement.

\[
\begin{align*}
\text{CH}_3 - & \text{O} - \text{CH}_2\text{CH}_2\text{CH}_3 \\
& 3 - \text{Methoxy propane}
\end{align*}
\]

\[
\begin{align*}
\text{HI} & \rightarrow \text{CH}_3\text{I} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \\
\text{HI} & \rightarrow \text{CH}_3\text{I} + \text{CH}_3\text{CH}_2\text{CH}_2\text{I} \\
\text{HI} & \text{excess}
\end{align*}
\]
Epoxides

Epoxides are compounds containing the three-membered ring.

\[
\begin{array}{c}
\text{O} \\
\text{C} - \text{C} - \\
\text{C}
\end{array}
\]  \quad \text{(Epoxide or oxirane ring)}

Epoxides belong to a class of compounds called cyclic ethers. The three-membered ring makes epoxides an exceedingly important class of compounds.

\[
\begin{array}{c}
\text{O} \\
\text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\
\text{1, 2 - Epoxybutane}
\end{array}
\quad \quad \quad \quad \quad \quad
\begin{array}{c}
\text{O} \\
\text{CH}_2 - \text{CH}_2 \\
\text{Epoxethane}
\end{array}
\]

PREPARATION

Epoxides are commonly obtained by oxidation of alkenes by peroxyc acids.

\[
\begin{array}{c}
\text{C} = \text{C} \\
\text{Alkene}
\end{array}
\quad \xrightarrow{\text{RCO}_2\text{H, Peroxycid}}
\quad \begin{array}{c}
\text{C} - \text{C} - \text{C} \\
\text{Epoxide}
\end{array}
\]

Silver oxide can also oxidise alkenes to epoxides. An internal S\text{N}2 reaction in a chlorohydrin can be used to prepare three membered cyclic ethers.

\[
\begin{array}{c}
\text{Cl} - \text{CH}_2 - \text{CH} - \text{CH}_3 \\
\text{OH}
\end{array}
\xrightarrow{\text{OH}^-}
\begin{array}{c}
\text{Cl} - \text{CH}_2 - \text{CH} - \text{CH}_3 - \text{Cl}^- \\
\text{O}
\end{array}
\xrightarrow{\text{O}}
\begin{array}{c}
\text{CH}_2 - \text{CH} - \text{CH}_3 \\
\text{1, 2 - Epoxypropane}
\end{array}
\]

Reactions: Epoxides have highly strained three-membered rings that can undergo acid- or base-catalysed ring cleavage.

1. **Acid-catalysed cleavage**

\[
\begin{array}{c}
\text{C} - \text{C} - \\
\text{Z:}
\end{array}
\quad \xrightarrow{\text{H}^+}
\quad \begin{array}{c}
\text{C} - \text{C} - \\
\text{Z}
\end{array}
\quad \xrightarrow{\text{OH}^-}
\quad \begin{array}{c}
\text{C} - \text{C} - \\
\text{Z}
\end{array}
\]

With \( Z = \text{nucleophile} \)

At first, the epoxide is protonated by an acid and the protonated epoxide can then undergo an attack by nucleophilic reagents.
2. Base-catalysed cleavage

\[
Z: + \overset{\text{C}}{-\overset{\text{C}}{-\overset{\text{O}}{\text{O}}}} \xrightarrow{\text{HZ}} \overset{\text{Z}}{\overset{\text{C}}{-\overset{\text{C}}{-\overset{\text{O}}{\text{O}}}}}
\]

Under alkaline conditions, an epoxide itself undergoes nucleophilic attack.

\[
\text{C}_2\text{H}_5\text{O}^-\text{Na}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OH}
\]

2-Ethoxyethanol

\[
\text{NH}_3 + \text{CH}_2 = \text{CH}_2 \rightarrow \overset{\text{H}_2\text{N}^-}{\overset{\text{CH}_2}{\text{CH}_2\text{OH}}}
\]

2-Aminoethanol

3. Reaction with Grignard reagent

\[
\overset{\text{R}}{\overset{\text{C}}{\text{O}}} + \text{CH}_2 = \text{CH}_2 \rightarrow \overset{\text{R}}{\overset{\text{C}}{\text{CH}_2\text{OMgX}}} \xrightarrow{\text{H}} \overset{\text{RCH}_2\text{CH}_2\text{OH}}{\text{Primary alcohol}}
\]

(Chain lengthened by two carbon atoms)

\[
\text{Phenyl magnesium bromide} + \overset{\text{O}}{\overset{\text{C}}{\overset{\text{H}}{\text{C}}}} \rightarrow \overset{\text{CH}_2\text{CH}_2\text{OMgBr}}{\text{Ethylene oxide}}
\]

2-Phenylethanol
MCQ

Q.1 Ethyl iodide reacts with moist Ag₂O to form—
(A) Ether (B) Alcohol (C) Alkene (D) Alkane

Q.2 Ethyl iodide reacts with sodium ethoxide to form—
(A) Ethene (B) Ethere oxide (C) Alcohol (D) None

Q.3 Ether reacts with halogen in dark and in light to give—
(A) Same products (B) Different products
(C) It does not react in light (D) It does not react in dark

Q.4 Ether reacts with PCl₅ to form—
(A) Ethyl chloride (B) Phosphorous oxy trichloride
(C) Both (A) & (B) (D) None

Q.5 An example of a compound with functional group — O — is—
(A) Acetic acid (B) Methyl alcohol (C) Diethyl ether (D) Acetone

Q.6 An organic compound A reacts with sodium metal and forms B. On heating with conc. H₂SO₄, A gives diethyl ether. So A and B are—
(A) C₃H₇OH and CH₃ONa (B) CH₃OH and CH₃ONa
(C) C₄H₇OH and C₄H₇ONa (D) C₂H₅OH and C₂H₅ONa

Q.7 In the presence of an acid catalyst, two alcohol molecules will undergo dehydration to give—
(A) Ester (B) Anhydride
(C) Ether (D) Unsaturated hydrocarbon

Q.8 A carbon compound A forms B with sodium metal and again A forms C with PCl₅, but B and C form diethyl ether. Therefore A, B and C are—
(A) C₂H₅OH, C₂H₅ONa, C₂H₅Cl (B) C₂H₅Cl, C₂H₅ONa, C₂H₅OH
(C) C₂H₅OH, C₂H₅, C₂H₅Cl₂ (D) C₂H₅OH, C₂H₅Cl, C₂H₅ONa

Q.9 When ethyl iodide is treated with dry silver oxide, it forms—
(A) Ag (B) C₂H₅OC₂H₅ (C) C₂H₅OH (D) COOH – COOH

Q.10 C–O–C bond angle in diethyl ether is about—
(A) 180° (B) 110° (C) 150° (D) 90°

ANSWER KEY

Q.1 (B) Q.2 (B) Q.3 (B) Q.4 (C) Q.5 (C) Q.6 (D) Q.7 (C) Q.8 (A) Q.9 (B) Q.10 (B)
**PHENOL (C₆H₅OH)**

Phenol is also known as carboxylic acid or Benzenol or hydroxy benzene. In phenol –OH group is attached to sp² – hybridised carbon. It was discovered by Runge in the middle oil fraction of coal tar distillation and named it carboxylic acid (carbo = coal; oleum = oil). It is also present in traces of human urine.

**METHODS OF PREPARATION**

1. **From Benzene sulphonlic acid:**
   When sodium salt of benzene sulphonlic acid is fused with NaOH phenol is obtained.
   \[ C₆H₅SO₃Na + NaOH \rightarrow C₆H₅OH + Na₂SO₃ \]

2. **From benzene diazonium chloride:**
   When benzene diazonium chloride solution is warmed phenol is obtained with evolution of nitrogen.
   \[ \text{NCl}^+ \xrightarrow{\text{H₂O}} \text{OH} + \text{N}_2 + \text{HCl} \]

3. **By distilling a phenolic acid:** with sodalime (decarboxylation):
   \[ \text{OH} \xrightarrow{\text{NaOH + CaO}} \text{OH} + \text{Na}_2\text{CO}_3 \]

4. **From Grignard reagent:** The grignard reagent on reaction with oxygen and subsequent hydrolysis by acid yields phenol.
   \[ C₆H₅MgBr \rightarrow C₆H₅OMgBr \rightarrow C₆H₅OH + MgBrOH \]

5. **From benzene:**
   \[ \text{-} + [\text{O}] \xrightarrow{\text{V₂O₅, 300°C}} \text{OH} \]

6. **Industrial preparation of phenol:** Phenol can be prepared commercially by:
   [a] Middle oil fraction of coal tar distillation
   [b] Raschig process
   [c] Dow's process
   [d] Cumene
[a] Middle oil fraction of coaltar:

\[\text{Coaltar} \xrightarrow{\text{Fractional distillation}} \text{Middle oil (172–230°C)}\]

\[\begin{align*}
\text{Cool} & \quad \text{(Phenol, cresols, Naphthalene)} \\
\text{Naphthalene} & \quad \text{(Solid crystals separate out)} \\
\text{Liquid} & \quad \text{NaOH} \\
& \quad \text{C}_6\text{H}_4\text{ONa} \\
& \quad \text{CO}_2\text{H}_2\text{O} \\
& \quad \text{C}_2\text{H}_5\text{OH} + \text{Na}_2\text{CO}_3
\end{align*}\]

[b] From cumene: (Isopropyl benzene): Cumene is oxidised with oxygen into cumene hydro peroxide in presence of a catalyst. This is decomposed by dil. H\(_2\)SO\(_4\) in to phenol and acetone.

\[
\begin{align*}
\text{CH}_3\text{CH}=(\text{CH}_3) & \xrightarrow{\text{O}_2, \text{Catalyst}} \text{O-CH}=(\text{CH}_3) \\
\xrightarrow{\text{NaOH, H}^+} & \text{OH} + \text{CH}_3-\text{C}-\text{CH}_3
\end{align*}
\]

[c] Raschig process: Chlorobenzene is formed by the interaction of benzene HCl and air at 300°C in presence of catalyst CuCl\(_2\) + FeCl\(_3\). It is hydrolysed by superheated steam at 425°C to form phenol and HCl.

\[
\begin{align*}
\text{C}_6\text{H}_6 + \text{HCl} + \frac{1}{2}\text{O}_2 & \xrightarrow{\text{CuCl}_2/\text{FeCl}_3, 300°C} \text{C}_6\text{H}_5\text{Cl} + \text{H}_2\text{O} \\
\text{C}_6\text{H}_5\text{Cl (steam)} + \text{H}_2\text{O} & \xrightarrow{425°C} \text{C}_6\text{H}_6\text{OH} + \text{HCl}
\end{align*}
\]

[d] Dow process: This process involves alkaline hydrolysis of chloro benzene

\[
\text{C}_6\text{H}_5\text{Cl} + \text{NaOH} \xrightarrow{\text{Cu-Fe, 300°C}} \text{C}_6\text{H}_6\text{OH} + \text{NaCl}
\]

**Physical Properties**

- Phenol is a colourless, hydroscopic crystalline solid.
- It attains pink colour on exposure to air and light.

\[
\text{C}_6\text{H}_5\text{OH} \quad \text{(Phenol, pink colour)}
\]

- It is poisonous in nature but acts as antiseptic and disinfectant.
- Phenol is slightly soluble in water, readily soluble in organic solvents.
- Solubility of phenol in water is much lower than alcohols because of larger hydrocarbon part in the molecule.
- Due to intermolecular H–Bonding, phenol has relatively high B.P. than the corresponding hydrocarbons, aryl halides etc.
CHEMICAL PROPERTIES

Chemical properties of phenol are classified in the following four categories.
Reactions of —H atom of —OH group.
Reactions of —OH group of phenol.
Reactions of Benzene ring.
Other Reactions.

Reactions of —H atom of —OH group

Acidic Nature: Phenol is a weak acid. The acidic nature of phenol due to formation of stable phenoxy ion in solution.

$$C_6H_5OH + H_2O \rightarrow C_6H_5O^- + H^+$$

The phenoxy ion is stable due to resonance.

- The negative charge is spread out over the benzene ring which is stabilising factor in the phenoxy ion.
- Electron withdrawing groups (—NO₂, —Cl) increase the acidity of phenol while electron releasing groups (—CH₃ etc.) decrease the acidity of phenol.
- Phenol is stronger acid than alcohols but weaker than the carboxylic acids and even carbonic acid.
- The acidic nature of phenol is observed in the following:
  [i] Phenol changes blue litmus to red.
  [ii] Highly electron positive metals react with phenol.
  $$2C_6H_5OH + 2Na \rightarrow 2C_6H_5ONa + H_2$$
  [iii] Phenol reacts with strong alkalis to form phenoxydes
  $$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$$
  [iv] However phenol does not decompose Na₂CO₃ or NaHCO₃ because phenol is weaker acid than carbonic acid.
  $$C_6H_5OH + Na_2CO_3 or NaHCO_3 \rightarrow No\ reaction$$

Reaction due to —OH group:

[1] Reaction with PCl₅: Phenol reacts with PCl₅ to form chloro benzene. The yield of chlorobenzene is poor and mainly triphenyl phosphate is formed.

$$C_6H_5OH + PCl_5 \rightarrow C_6H_5Cl + POCl_3 + HCl$$

$$3C_6H_5OH + 5POCl_3 \rightarrow (C_6H_5)₃PO_4 + 2HCl$$

[2] Reaction with Zn dust: When phenol is distilled with zinc dust benzene is obtained.

$$C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO$$


$$C_6H_5OH + NH_3 \rightarrow C_6H_5NH_2 + H_2O$$

[4] Reaction with FeCl₃: Phenol gives violet colouration with FeCl₃ solution (neutral) due to formation of a complex.

$$C_6H_5OH + FeCl_3 \rightarrow Voilet\ colour$$

- This reaction is used to differentiate phenol from alcohols.
[5] **Acetylation**: Phenol reacts with acid chlorides or acid anhydrides in alkali solution to form phenyl esters.

\[
\text{C}_6\text{H}_5\text{OH} + \text{ClCOCH}_3 \xrightarrow{\text{NaOH}} \text{C}_6\text{H}_5\text{OC}-\text{CH}_3
\]

\[
\cdot \text{C}_6\text{H}_5\text{OH} + \text{Cl}-\text{C}-\text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{O}--\text{C}_6\text{H}_5
\]

This reaction is called **Schotten–Baumann reaction**.


\[
\text{C}_6\text{H}_5\text{OH} + \text{NaOH} \rightarrow \text{C}_6\text{H}_5\text{ONa} \xrightarrow{\text{RX}} \text{C}_6\text{H}_5\text{OR}
\]

\[
\cdot \text{C}_6\text{H}_5\text{OH} + \text{CH}_2\text{N}_2 \rightarrow \text{C}_6\text{H}_5\text{OCH}_3 + \text{N}_2
\]

[7] **Reaction with P_2S_5**:

\[
5\text{C}_6\text{H}_5\text{OH} + \text{P}_2\text{S}_5 \rightarrow 5\text{C}_6\text{H}_5\text{SH} + \text{P}_2\text{O}_5
\]

**Reaction of Benzene Ring**: The –OH group is ortho and para directing. It activates the benzene nucleus.

[1] **Halogenation**: Phenol reacts with bromine in CCl_4 to form mixture of o- and p-bromo phenol.

\[
\text{OH} + \text{Br}_2 \rightarrow \text{OH} + \text{Br} + \text{OH} + \text{Br}
\]

\[
\cdot \text{Phenol reacts with bromine water to from a white ppt. of 2, 4, 6 tribromo phenol.}
\]

\[
\text{OH} + 3\text{Br}_2 \rightarrow \text{Br} + \text{Br} + \text{3HBr}
\]

[2] **Nitration**:

[a] Phenol reacts with dil. HNO_3 at 5–10°C to form o- and p- nitro phenols.

\[
\text{OH} \xrightarrow{\text{Dil. HNO}_3, \text{5–10°C}} \text{OH} + \text{NO}_2
\]

(40%) (10%)

[b] When phenol is treated with conc. HNO_3 in presence of conc. H_2SO_4 2,4,6-trinitro phenol (picric acid) is formed.


[6] Reimler–Tiemann reaction: Phenol on refluxing with chloroform and NaOH (aqueous) followed by acid hydrolysis yields o-hydroxy benzaldehyde. When CCl$_4$ is used salicylic acid is formed.
Kolbe's Schmidt reaction: This involves the reaction of \( C_6H_5ONa \) with \( CO_2 \) at 140°C followed by acid hydrolysis, salicylic acid is formed.

\[
\text{ONa} + CO_2 \xrightarrow{140^\circ C} \text{O} \xrightarrow{\text{acetylation}} \text{O} \xrightarrow{\text{H}_2O} \text{O} \xrightarrow{120^\circ C} \text{O} \xrightarrow{\text{H}_2O} \text{OH} \xrightarrow{\text{COONa}} \text{Salicylic acid}
\]

Hydrogenation: Phenol when hydrogenated in presence of Ni at 150-200°C forms cyclohexanol.

Fries rearrangement reaction:
When phenyl ester is heated in nitrobenzene solution, in the presence of anhy. \( AICl_3 \) then rearrangement takes place in which acyl group is transferred at \( o- \) & \( p- \) positions of phenolic group. Up to 60°C, para product is obtained mainly and above 160°C ortho products are obtained as major product.

Duff's reaction:

\[
\begin{align*}
\text{OH} + (\text{CH}_2\text{N}_3) & \xrightarrow{\text{C}_6\text{H}_5\text{COCH}_3} \xrightarrow{60^\circ C} \text{C}_6\text{H}_5\text{COCH}_3 \\
\text{C}_6\text{H}_5\text{OCOCH}_3 & \xrightarrow{\text{Ac}\text{-Cl}, \text{HNO}_3} \xrightarrow{100^\circ C} \text{C}_6\text{H}_5\text{COCH}_3
\end{align*}
\]

(Hexamethylene tetraamine)

Coupling reactions:

Phenol couples with benzene diazonium chloride in presence of an alkaline solution to form a dye(p-hydroxy azobenzene)

\[
\begin{align*}
\text{ON} & \xrightarrow{\text{N}_2\text{Cl}} \xrightarrow{\text{OH}^-} \text{ON} \xrightarrow{\text{OH}^-} \text{ON} \xrightarrow{\text{OH}^-} \text{ON}
\end{align*}
\]
[b] Phenol couples with phthalic anhydride in presence of conc. H₂SO₄ to form a dye (phenolphthalein)

\[
\begin{align*}
\text{O} & \quad \text{C} & \quad \text{O} \quad \text{H} & \quad \text{O} & \quad \text{OH} \\
\text{O} & \quad \text{OH} & \quad \text{H} & \quad \text{O} & \quad \text{OH} \\
\text{O} & \quad \text{OH} & \quad \text{H} & \quad \text{O} & \quad \text{OH} \\
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{C} & \quad \text{O} \quad \text{H} & \quad \text{O} & \quad \text{OH} \\
\text{O} & \quad \text{OH} & \quad \text{H} & \quad \text{O} & \quad \text{OH} \\
\text{O} & \quad \text{OH} & \quad \text{H} & \quad \text{O} & \quad \text{OH} \\
\end{align*}
\]

Condensation with formaldehyde: Phenol condenses with HCHO (excess) in presence of NaOH to form a polymer known as bakelite.

\[
\begin{align*}
\text{OH} & \quad \text{+ HCHO} \quad \rightarrow \quad \text{OH} \\
(40\%) & \quad \text{CHOH} & \quad \text{OH} \\
(20\%) & \quad \text{OH} & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{OH} \\
\end{align*}
\]

Polymer bakelite (Phenol formaldehyde resin)

[13] Liberman's nitroso reaction: When phenol is reacted with NaNO₂ and conc. H₂SO₄ it gives a deep green or blue colour which changes to red on dilution with water. When made alkaline with NaOH original green or blue colour is restored.

The reaction is used as a test of phenol.

\[
2\text{NaNO}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{HNO}_2 + \text{Na}_2\text{SO}_4
\]

\[
\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{[F - HO]NO} & \quad \text{OH} \\
\text{N - OH} & \quad \text{Quinone mono-oxide (Red colour)}
\end{align*}
\]

\[
\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{CH}_3 & \quad \text{C - CH}_3 & \quad \text{Bis - Phenol-A} \\
\text{p-p' isopropylidene diphenol}
\end{align*}
\]

[14] Reaction with acetone:
Oxidation:
[1] In presence of air:

\[
\text{OH} \xrightarrow{\text{KIO}_3} \text{O} \xrightarrow{\text{Benzoquinone (red)}} \text{OH}
\]

[2] KMnO\(_4\):

\[
\text{OH} \xrightarrow{\text{meso tartaric acid}} \text{CH(OH) COOH}
\]

Test of Phenol:
[1] Phenol turns blue litmus to red.

\[
\text{Phenol in conc. } \text{H}_2\text{SO}_4 \xrightarrow{\text{NaNO}_2, \text{excess of water}} \text{Red colour} \xrightarrow{\text{NaOH, excess}} \text{Blue colour}
\]


Differences between phenol and alcohol (C\(_2\)H\(_5\)OH):
[1] Phenol is more acidic than aliphatic alcohol due to resonance in phenoxyide ion.
[2] Phenol gives violet colour with FeCl\(_3\), while aliphatic alcohol does not give.
[3] Phenol gives triphenyl phosphate with PCl\(_3\), while aliphatic alcohol gives alkyl chloride.
[4] Phenol has phenolic odour whereas alcohol has pleasant odour.
[5] Phenol on oxidation gives quinone while alcohol gives aldehyde or ketone and acids.

Uses of Phenol:
Phenol is used:
[1] As an antiseptic in soaps and lotions.
[2] In manufacture of azodyes, phenolphthalein, picric acid (explosive), cyclohexanol (Solvent for rubber), plastic (bakelite) etc.
[3] In manufacture of drugs like aspirin salol, phenacetin etc.
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Test/Reaction</th>
<th>Alcohol</th>
<th>Phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Litmus test</td>
<td>No Reaction</td>
<td>Blue litmus red</td>
</tr>
<tr>
<td>2.</td>
<td>FeCl₃ Solution</td>
<td>No Reaction</td>
<td>Violet colour</td>
</tr>
<tr>
<td>3.</td>
<td>Benzene diazonium salt</td>
<td>No Reaction</td>
<td>Yellow or orange azo dye</td>
</tr>
<tr>
<td>4.</td>
<td>Br₂ water</td>
<td>No Reaction</td>
<td>2, 4, 6-tribromophenol</td>
</tr>
</tbody>
</table>

**MCQ**

**Q.1** In chlorobenzene, the — Cl group -
(A) Activates the benzene ring more, via resonance effect than deactivating it via inductive effect.
(B) Deactivates the benzene ring more, via inductive effect than activating it via resonance effect.
(C) Activates the benzene ring via resonance effect and deactivates it via inductive effect. Both these effect are evenly matched.
(D) It is a net deactivating group with director characteristics.

**Q.2** Identify 'Z' in the reaction given below -

![Reaction](image)

(A) ![Compound A](image)  (B) ![Compound B](image)  (C) ![Compound C](image)  (D) ![Compound D](image)

**Q.3** The correct order of reactivity towards electrophilic substitution is -
(A) Phenol > Benzene > Chlorobenzene > Benzoic acid
(B) Benzoic acid > Chlorobenzene > Benzene > Phenol
(C) Phenol > Chlorobenzene > Benzene > Benzoic acid
(D) Benzoic acid > Phenol > Benzene > Chlorobenzene

**Q.4** Which among the following is the strongest o-, p-directing group in benzene is -
(A) –OH  (B) –Cl  (C) –OCH₃  (D) –CH₃

**Q.5** The compound represented by the molecular formula C₇H₈O are -
(A) Only alcohol  (B) Only ether
(C) Only phenolic compound  (D) All the three types of compounds
Q.6 Indenify A, B, and C in the following reactions—

(a) \( \text{OH} \quad \xrightarrow{\Delta} \quad \text{OH} \)

(b) \( \text{OH} \quad \xrightarrow{\Delta} \quad \text{B} \)

(c) \( \text{C} \quad \xrightarrow{\text{C}_2\text{H}_5} \quad \text{OC}_2\text{H}_5 \)

(A) Sodalime, benzene, potassium phenoxide
(B) Zn, benzene, sodium ethoxide
(C) Zn, cyclohexanone, sodium ethoxide
(D) None of the above

Q.7 Water insoluble aromatic compound dissolves in sodium hydroxide but remain insoluble in sodium bicarbonate. Hence the expected compound should be - [where \( \phi = \text{C}_6\text{H}_5 \)]

(A) \( \phi - \text{COOH} \)  (B) \( \phi - \text{OH} \)  (C) \( \phi - \text{CO} - \text{CH}_3 \)  (D) \( \phi - \text{NH}_2 \)

Q.8 Salicylaldehyde and o-nitrophenol are less soluble in water because -

(A) Their molecular weights are high  (B) They exhibit intra molecular H-bonding
(C) They are aromatic compounds  (D) \(-\text{CHO}\) and \(-\text{NO}_2\) groups are not polar

Q.9 Rate of substitution reaction in phenol is -

(A) Slower than the rate of benzene  (B) Faster than the rate of benzene
(C) Equal to the rate of benzene  (D) None

---

**ANSWER KEY**

Q.1  (B)  Q.2  (C)  Q.3  (A)  Q.4  (A)  Q.5  (D)
Q.6  (A)  Q.7  (B)  Q.8  (B)  Q.9  (B)
OXIDATION OF ALKENES, ALCOHOLS & CARBONYL COMPOUNDS

(I) OXIDATION OF ALKENES

\[
\begin{align*}
R-\text{CH}=&-\text{CR}_2 & \xrightarrow{\text{OsO}_4} & R-\text{CH}_2-\text{CR}_2 \\
& & & + \text{OH} \quad \text{OH} \\
& & & \text{Cold dil. alkaline} \\
& & & \text{KMnO}_4 \\
& & & \text{OH} \quad \text{OH}
\end{align*}
\]

- Cold dil. alkaline KMnO\(_4\) is called as Bayer's reagent.
- Overall syn addition
- Given by alkenes & alkynes
- Benzene & Cyclopropane can not give this reaction.

If we use acidic KMnO\(_4\) or warm KMnO\(_4\) or too concentrated KMnO\(_4\) the oxidative cleavage of Glycol occurs resulting in mixture of Carboxylic acids & Ketones.

\[
R-\text{CH} = C\text{R}_2 \xrightarrow{\text{H}^+, \text{KMnO}_4} \Delta \text{RCOOH} + \text{R}_2\text{C} = \text{O}
\]

Hot acidic KMnO\(_4\), Hot acidic K\(_2\)Cr\(_2\)O\(_7\), & hot acidic NaO\(_4\) gives same result with alkene. The effect is similar to that of oxidative ozonolysis on alkenes.

Prellschaive reaction:
Epoxidation of alkenes is reaction of alkenes with peroxyciids.

\[
\begin{align*}
\text{CH}_2=\text{CH}_2 + \text{CH}_3-\text{C}-\text{O}-\text{O}-\text{H} & \rightarrow \text{CH}_2=\text{CH}_2 + \text{CH}_3-\text{C}-\text{OH} \\
\end{align*}
\]

- With the decrease in nucleophilicity of double bond, rate of reaction decreases.
- With the decrease in \(\Theta\) withdrawing substituents in leaving group, rate decreases.
(II) OXIDATION OF ALCOHOLS

Oxidising agents

1) Cu / 300°C (or Red hot Cu tube)

3) H⁺/K₂Cr₂O₇, Δ (Strong oxidising agent)

2) H⁺/KMnO₄, Δ (Strong oxidising agent)

4) PCC (Pyridinium chloro chromate)

5) Collin’s reagent

(2 mol) + CrO₃ + CH₂Cl₂

6) Sarett reagent (i.e. PCC in CH₂Cl₂)

7) PDC

(Pyridinium dichromate)

8) Jones reagent (H₂CrO₄ in Anhydrous acetone)

or CrO₃ + H₂SO₄ in acetone.
Sufficiently mild so that it oxidises alcohols without oxidising or rearranging double bonds (8 or 9)

9) TsCl + DMSO + NaHCO₃

RCH₂OH[TrCl] → RCH₂OTs[NaHCO₃] → RCHO

R₂CHOH[TrCl] → R₂CH-OTs[NaHCO₃] → R₂CO

R₃COH[TrCl] → R₃C-OTs[NaHCO₃] → X

10) MnO₂ Oxidises only allylic or benzylic-OH i.e.

1st Allylic or benzylic OH → MnO₂ → Aldehyde

2nd Allylic or benzylic OH → MnO₂ → Ketone

No effect on 3rd ROH and on Carbon-carbon multiple bond.

11) Periodic cleavage

A similar oxidation is obtained in case of HIO₄ known as periodic cleavage.

12) NBS

Openau oxidation

R-CH-OH + HO-IO → R-CH₂OIO⁻ + H⁺

But reaction is only observed for cis Vic-diols.

R₂C-OH + HO-IO → R₂C=O + HIO₃

(R₂CH-O)₃Al-O⁻ + 3Me₃C=O + Al

(R₂CH-O)₃Al-O⁻ + 3Me₃C=O + Al

Oxidation of alcohol with aluminium tertiary butoxide is Openau oxidation.

R₂CH-OH + Al(OCH₂Me)₃ → \[\text{Me₃C=O} + \text{Al} \]
Different oxidising agents are used to oxidise alcohols in corresponding carbonyl compounds and carboxylic acids.

\[
\text{e.g. (I)} \quad R - CH_2 - OH \xrightarrow{\text{mild oxidising agent}} R - C - H (\text{Aldehyde})
\]

Oxidation agent: 1, 4, 5, 6, 7, 8, 9, 12

\[
\text{(II)} \quad R - CH - R' \xrightarrow{\text{mild oxidising agent}} R - C - R' (\text{Ketone})
\]

Oxidation agent: 1, 2, 3, 4, 5, 6, 7, 8, 9, 12, 13

\[
\text{(III)} \quad R - CH_2 - OH \xrightarrow{\text{strong oxidising agent}} R - C - OH
\]

Oxidation agent: 2, 3

\[
\text{(IV)} \quad \text{CH}_3 - \text{C} - \text{OH} \xrightarrow{\text{Cu, } 300^\circ \text{C}} \text{CH}_3 - \text{C} - \text{CH}_3
\]

Dehydration takes place.

(V) Double bond or Triple bond is not affected by 1, 4, 5, 6, 7, 8, 9, 10

(VI) No effect on 3° alcohol by 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13

(III) Oxidation of Carbonyl Compounds

1. \(\text{RCHO} + [\text{Ag(NH}_3\text{)}_2\text{]OH} \xrightarrow{\Delta} \text{RCOOH} + \text{NH}_3 + \text{Ag}\downarrow\)

   Aldehyde acts as reducing agent, they can reduce mild oxidising agents like Tollen's Reagent. Tollen's test Gentle heating for 20 to 25 mins.

2. FeHling's Solutions

   FeHling's A
   FeHling's B
   FeHling's C
   FeHling's D
   FeHling's E
   FeHling's F
   FeHling's G
   FeHling's H
   FeHling's I
   FeHling's J
   FeHling's K
   FeHling's L
   FeHling's M
   FeHling's N
   FeHling's O
   FeHling's P
   FeHling's Q
   FeHling's R
   FeHling's S
   FeHling's T
   FeHling's U
   FeHling's V
   FeHling's W
   FeHling's X
   FeHling's Y
   FeHling's Z

   aq. CuSO_4
   Alk. solution of Roschelye salt (sodium potassium tartrate)
   It acts as a carrier for Cu^{2+} as it makes reversible complex with Cu^{2+}

   This test is also used in Blood and Urine test.

   \[
   \text{RCHO} + \text{Cu}^{2+} \xrightarrow{\Delta} \text{RCOOH} + \text{Cu}^+ \xrightarrow{\Delta} \text{RCOO}^- \xrightarrow{\Delta} \text{Cu}_2\text{O} \text{(red ppt.)}
   \]

3. Benedect's solution

   Sodium Citrate + NaOH + NaHCO_3 + CuSO_4

   \[
   \text{RCHO} + \text{Cu}^{2+} \xrightarrow{\Delta} \text{RCOOH} + \text{Cu}^+ \xrightarrow{\Delta} \text{RCOO}^- \xrightarrow{\Delta} \text{Cu}_2\text{O} \text{(red ppt.)}
   \]

4. \(\text{RCHO} + \text{HgCl}_2 + \text{H}_2\text{O} \xrightarrow{\Delta} \text{RCOOH} + 2\text{HCl} + \text{Hg}_2\text{Cl}_2\)

   \[
   \text{RCHO} + \text{Hg}_2\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{RCOOH} + 2\text{HCl} + 2\text{Hg} \downarrow \text{grey ppt.}
   \]
5. **Schiff's Reagent**

Schiff's Reagent is aq. solution of following base decolourised by passing SO₂. Aldehyde restore pink colour of Schiff's reagent.

\[
\text{NH}_2 \quad \text{NH}_2 \\
\text{SO}_2 \quad \text{Colourless solution} \quad \text{RCHO} \quad \Delta \quad \text{RCOOH + Pink colour}\]

(Schiff's Reagent)

*P-Rosaniline Hydrochloride*

Magenta colour (Fuschin)

Ketones are not easy to oxidize so they do not give these 5 tests. These five tests can be used to distinguish aldehyde and ketones. Both gives 2,4 DNP test

**KETONES ARE DIFFICULT TO OXIDIZE**

Ketones can be oxidized from their enolic form at high temperature with very strong oxidizing agent. Oxidation of ketones is sometimes governed by Popoff's rule. According to this rule carbonyl group remains with the smaller alkyl group. More electron rich alkene will be easy to oxidized.

\[
\text{Me - C - Me} \quad \frac{[O]}{\Delta} \quad \text{MeCOOH + CO}_2 + \text{H}_2\text{O}
\]

** Allylic oxidation**

SeO₂ is a selective oxidizing agent with converts –CH₂– group adjacent to carbonyl group into carbonyl group. The reagent, in general, oxidises active methylene and methyl groups to ketonic and aldehydic groups respectively.

\[
\text{CH}_3 = \text{CH} - \text{CH}_2 \quad \text{SeO}_2 \quad \text{CH}_2 = \text{CH} - \text{CH}_2
\]

Rate of reactivity order 2° C – H > 1° C – H > 3° C – H

\[
\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 \quad \text{SeO}_2 \quad \text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 \\
\text{OH}
\]

\[
\text{CH}, \quad \text{SeO}_2 \quad \text{HO-CH}_2, \quad \text{CH} - \text{CH}, \quad \text{CH}_3
\]

\[
\text{HO} \quad \text{SeO}_2 \quad \text{HO-CH}_2, \quad \text{CH} - \text{CH}, \quad \text{CH}_3
\]
### Reducing agents and their role

<table>
<thead>
<tr>
<th>Group</th>
<th>Product</th>
<th>LAH in ether</th>
<th>LiAlH₄(OCMe₃)₃ in THF</th>
<th>NaBH₄ in EtOH</th>
<th>H₂⁺ <strong>catalyst</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>-CHO</td>
<td>-CH₂OH</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>&gt;C=O</td>
<td>&gt;CH-OH</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>-CO₂H</td>
<td>-CH₂OH</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
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<td>-CO₂R</td>
<td>-CH₂OH</td>
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<td>-</td>
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<td>+</td>
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<tr>
<td>-COCl</td>
<td>-CH₂OH</td>
<td>+</td>
<td>+*</td>
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<td>-CONH₂</td>
<td>-CH₂NH₂</td>
<td>+</td>
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<td>+</td>
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<td>(RCO)₂O</td>
<td>RCH₂OH</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
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<tr>
<td>-CN</td>
<td>-CH₂NH₂</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>&gt;C=NOH</td>
<td>-CH₂NH₂</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>&gt;C=C&lt;</td>
<td>&gt;CH-CH&lt;</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>&gt;C=C-</td>
<td>&gt;CH-CH-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>¹° RX</td>
<td>RH</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>

* Product is RCHO
** Catalyst: Ni / Pd / Pt / Ru

### LiAlH₄ as a reducing agent

(i) \[ \text{C} = \text{O} \xrightarrow{(1) \text{LiAlH}_4} \text{C} = \text{O} \xrightarrow{\text{From LAH}} \]

(ii) \[ \text{R} - \text{C} - \text{NH}_2 \xrightarrow{(1) \text{LiAlH}_4} \text{R} - \text{CH}_2 - \text{NH}_2 \]

(iii) \[ \text{R} - \text{C} - \text{OR'} \xrightarrow{(1) \text{LiAlH}_4} \text{R} - \text{CH}_2 - \text{OH} + \text{R'} - \text{OH} \]

(iv) \[ \text{R} - \text{C} = \text{N} \xrightarrow{(1) \text{LiAlH}_4} \text{R} - \text{CH}_2 - \text{NH}_2 \]

(v) \[ \text{R} - \text{C} - \text{OH} \xrightarrow{(1) \text{LiAlH}_4} \text{R} - \text{CH}_2 - \text{OH} \]

**Wolf Kischner reduction:**
\[ \text{C} = \text{O} \xrightarrow{\text{NH}_2-\text{NH}_2/\text{OH}^-} \text{CH}_2 + \text{N}_2 \]

**Clemenson reduction**
\[ \text{C} = \text{O} \xrightarrow{\text{Zn(Hg)}} \xrightarrow{\text{HCl(conc.)}} \text{CH}_2 \]