

# ALCOHOL

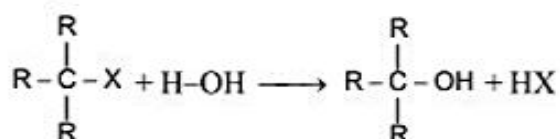
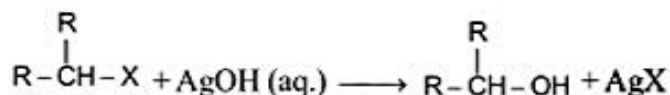
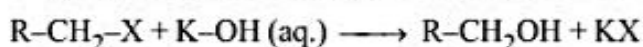
## INTRODUCTION

- (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  $C_nH_{2n+1}OH$  or  $C_nH_{2n+2}O$ .
- (d) The hybridisation state of carbon is  $sp^3$ .
- (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.  $C_2H_5OH$
  - (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

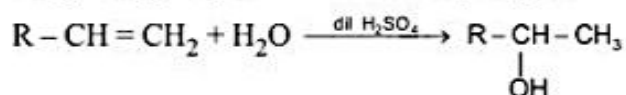
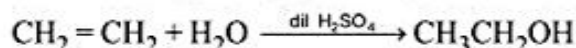
### From Alkyl halides :

Alkyl halides reacts with aq. KOH/aq. AgOH or  $H_2O$  and forms alcohol.



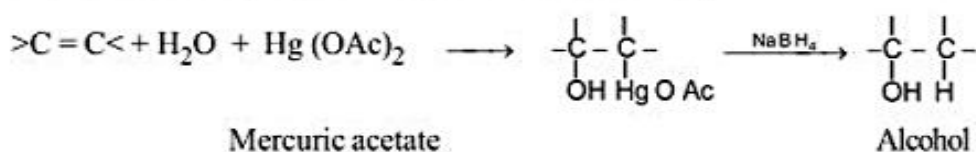
### From Alkenes :

**Hydration** – Alkenes are catalytically hydrated by dilute mineral acid solution.



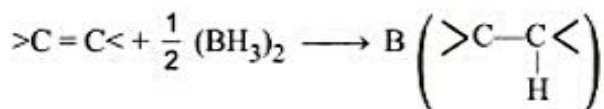
### Oxymercuration – demercuration :

Alkenes react with mercuric acetate in the presence of water to give hydroxymercurial compounds, which on reduction yield alcohols. (Markovnikov addition)

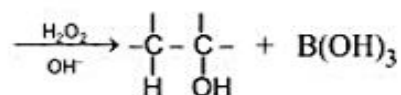
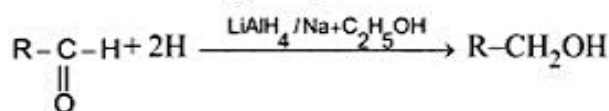


**Hydroboration – Oxidation :**

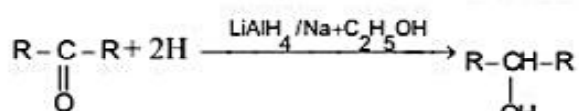
(Anti-Markownikov orientation)



Alkene      Diborane                  Tri alkyl borane

**By Reduction of Carbonyl compounds :-**

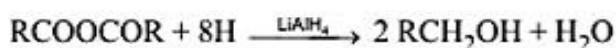
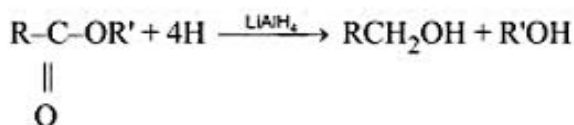
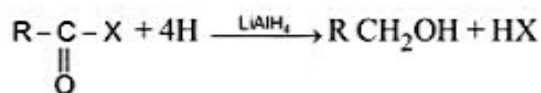
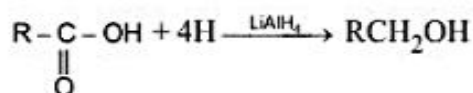
1° alcohol



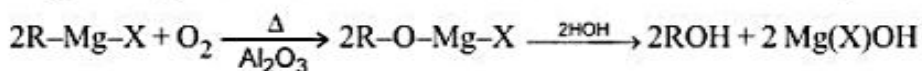
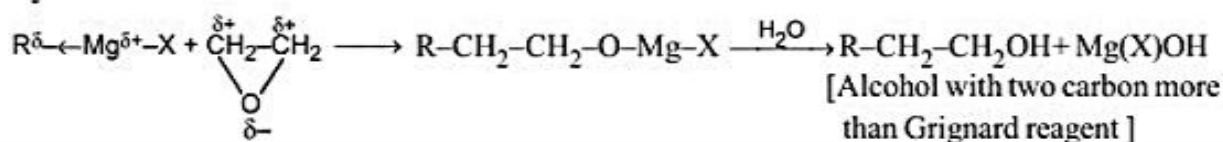
2° alcohol

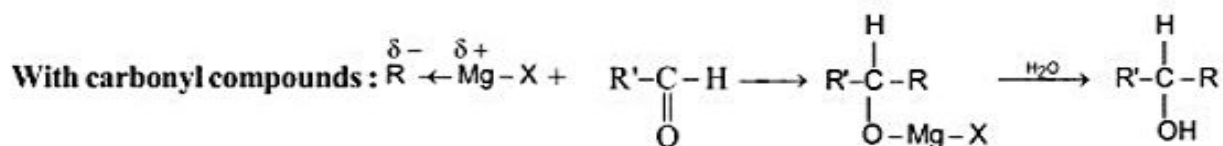
**Note :**

- (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'.

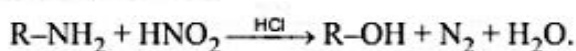
**By Reduction of Acid & its derivatives :****Important Note :-** Acid amide does not form alcohol on reduction. It forms primary amine.**From Grignard reagent :****With oxygen :-**

Grignard reagent forms alcohol of same no. of carbon atoms as in Grignard reagent.

**With ethylene oxide :**

**Note :**

- (i) If  $R' = H$ , Product will be 1° alcohol.
- (ii) If  $R' = R$ , 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 :-**

But it is not a good method for preparation of alcohol because a number of by products 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  $\propto$  molecular mass  $\propto \frac{1}{\text{No. of branches}}$
- (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 :-

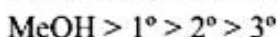
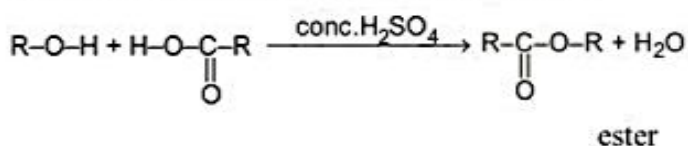
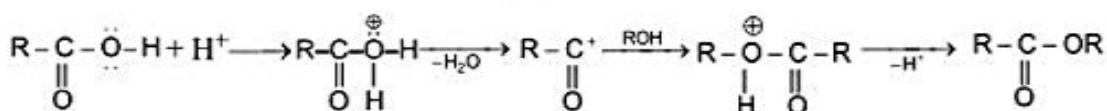
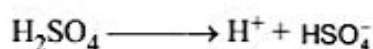
- (i) Reaction of H atom of -OH group of Alcohols
- (ii) Reaction of OH group of Alcohols
- (iii) General reaction of Alcohols.

**Reaction of H atom of -OH group of Alcohols :**

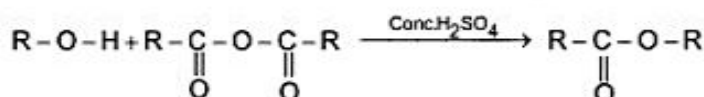
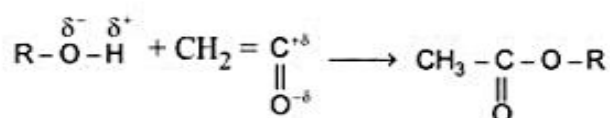
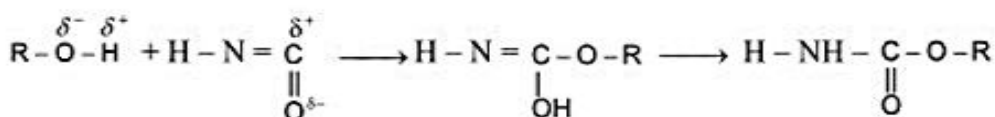
These are the reactions in which alcohol shows acidic character.

**Reaction with Na :**

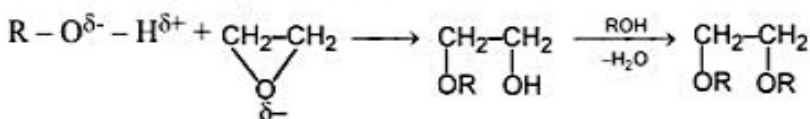
The acidic order of alcohols is

**Esterification / Reaction with carboxylic acid:-****Mechanism :**

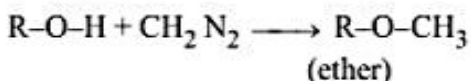
**Note :** The above reaction is laboratory method of ester preparation.

**Reaction with Acid derivatives :****Reaction with Ketene :-****Reaction with Isocyanic Acid :-**

amino ester (urethane)

**Reaction with ethylene oxide :**

1,2-dialkoxy ethane

**Reaction with Diazomethane :-**

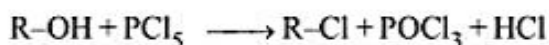


## Reaction of –OH group of Alcohols :-

### Reaction with dry HX (Grove's Process) :



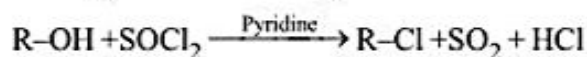
### Reaction with $PCl_5$ :



### Reaction with $PCl_3$ :



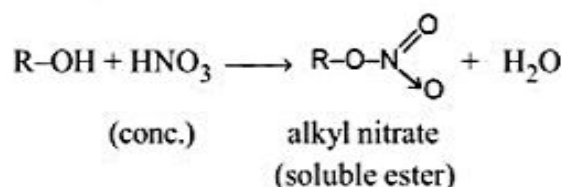
### Reaction with $SOCl_2$ (Darzen reaction) :



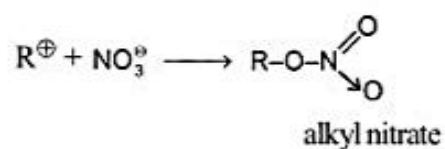
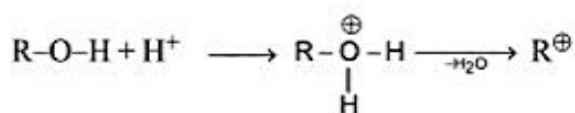
### Reaction with ammonia :



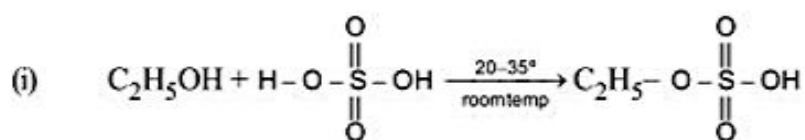
### Reaction with $HNO_3$ :



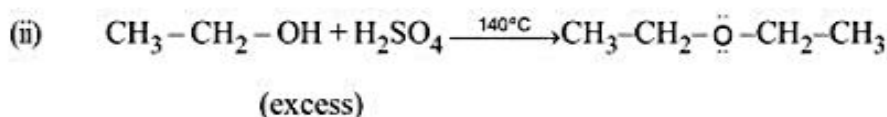
### Mechanism :-

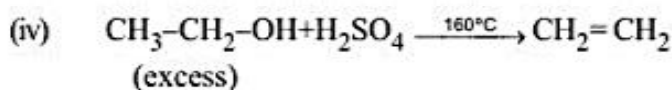
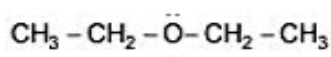
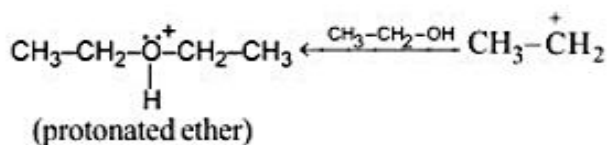
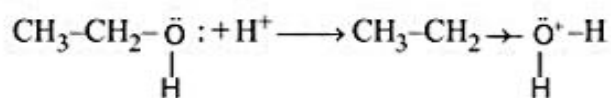
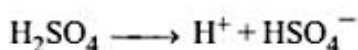
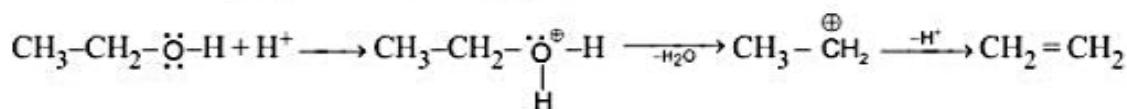
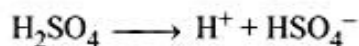


### Reaction with $H_2SO_4$ :-

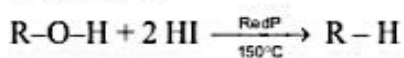


stable upto (80-100°C)

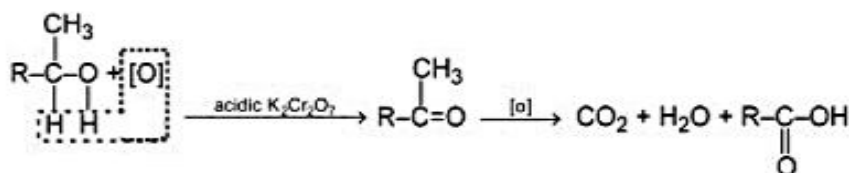
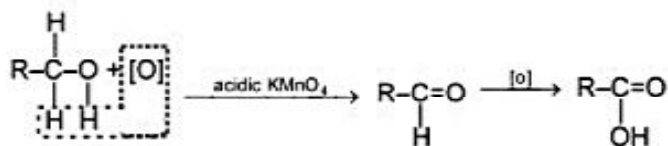


**Mechanism :-****Mechanism :-**

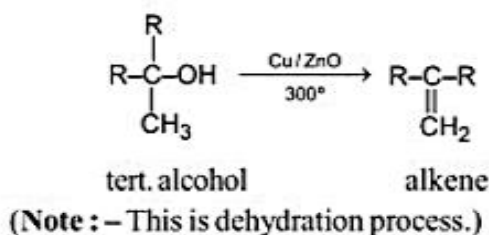
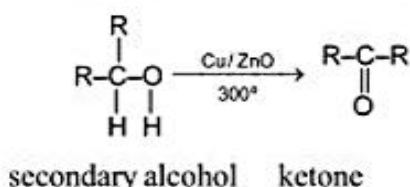
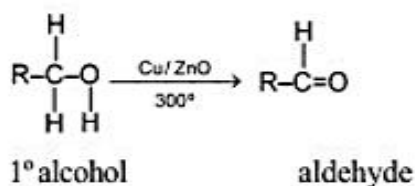
**Note :** In the above reaction excess of ethanol is present so, intermediate carbocation satisfies itself by elimination.

**GENERAL REACTION OF ALCOHOLS****Reduction :-**

Reacting species of solution is  $\text{HCrO}_4^-$ .

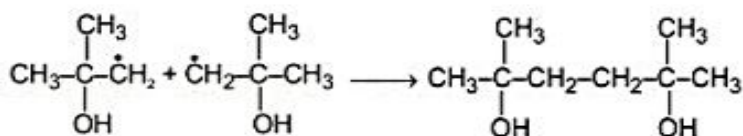
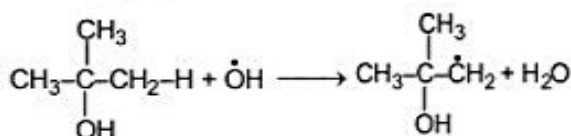
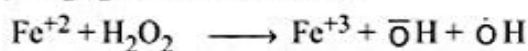


### Catalytic Oxidation / Dehydrogenation :



### Oxidation through Fenton's Reagent :

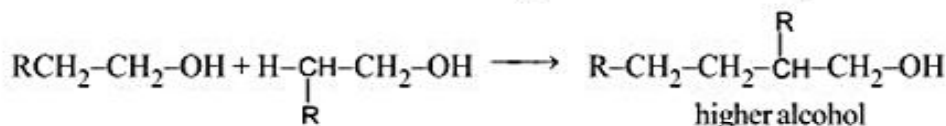
Higher and branched alcohols are converted into diols through Fentons reagent. ( $\text{FeSO}_4 + \text{H}_2\text{O}_2$ ) is Fenton's reagent.



2,5-dimethyl hexandiol-2,5

### Self Condensation :

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

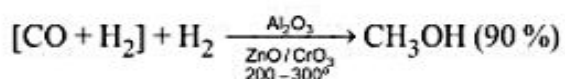


Note : The above reaction is called as 'Guerbet's Reaction'.

### Preparation of methanol :

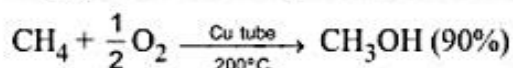
Methanol is also called as carbinol or wood spirit.

#### From Water Gas :

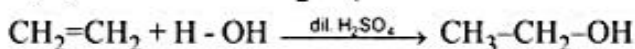


**From Methane : -**

CH<sub>4</sub> gives methanol on partial oxidation in Cu tube.

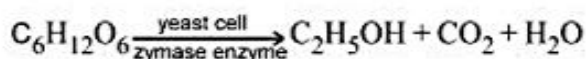
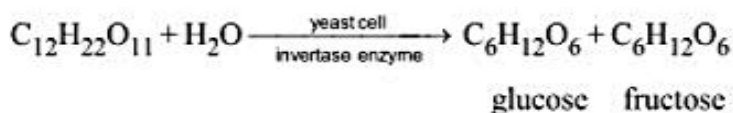
**Preparation of Ethanol :****From Ethene :**

By hydration with dil. H<sub>2</sub>SO<sub>4</sub>

**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.

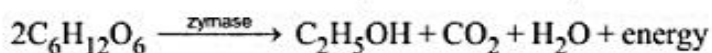
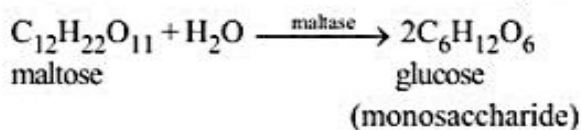
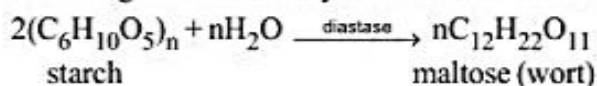


**Note:** Glucose and fructose are functional isomers.

**Preparation of ethanol from starch :**

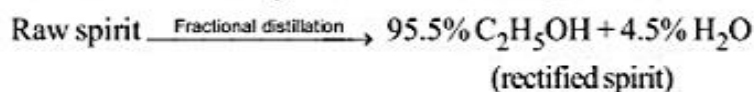
(i) Starch solution is technically called 'Mash'

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

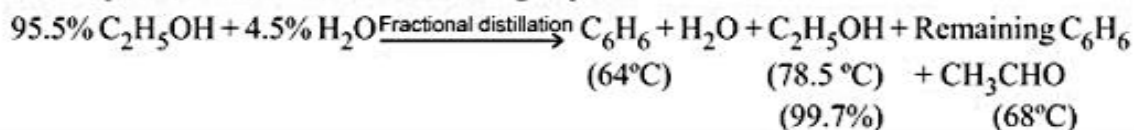


(iii) From both of the methods conc. of ethanol achieved is 10-12% which is called 'Wash'.

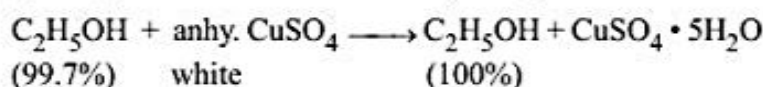
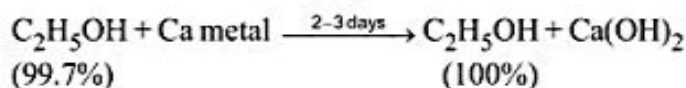
(iv) Distillation of wash is done in special apparatus 'Coffee's still', which is based on counter current method. From this distillation yield of alcohol is 90%, which is called Raw spirit.



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







## 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.

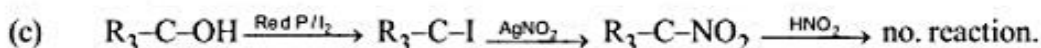
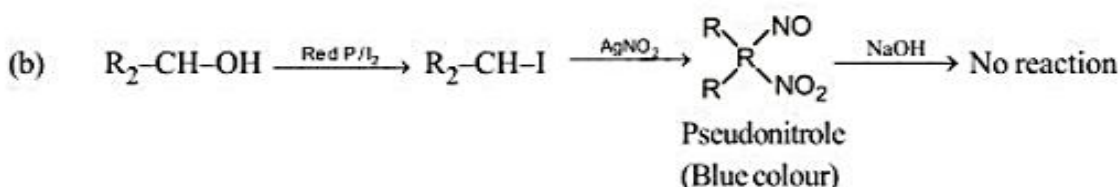
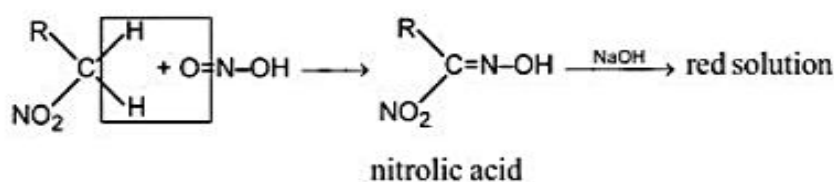
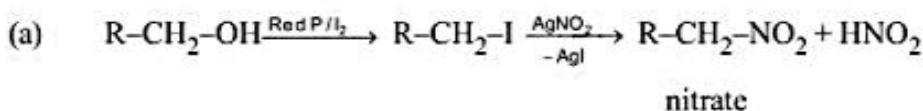
**By Catalytical Oxidation / Dehydrogenation :** Primary alcohol gives aldehyde on oxidation, secondary alcohol gives ketone and tertiary alcohol gives alkene (dehydration takes place in this condition to tertiary alcohols.)

**Lucas Test :** A mixture of (anhydrous  $\text{ZnCl}_2$  + Conc.  $\text{H}_2\text{SO}_4$ ) is called as **Lucas Reagent**.

- (i) 3° alcohol gives white ppt. with lucas reagent in 2-3 seconds only.
- (ii) 2° alcohol takes 9 - 10 minutes.
- (iii) 1° alcohol does not gives white ppt. at room temperature.

**Victor Meyer Test : -**

This test is also known as RBW ( Red, Blue, White) test.



### Difference between Methanol and Ethanol

| Methanol   | Ethanol                                    |
|--|--|
| 1. When $\text{CH}_3\text{OH}$ is heated on Cu coil it gives formalin like smell.  | Ethanol does not give formalin like smell. |
| 2. When $\text{CH}_3\text{OH}$ is heated with salicylic acid in $\text{H}_2\text{SO}_4$ (conc.) then methyl salicylate is formed which has odour like winter green oil | No such odour is given by ethanol          |
| 3. It does not give haloform or Iodoform test.   | It gives haloform test.                    |

### MCQ

- Q.1** Which of the following reaction is called as 'Bouveault-Blanc reduction' -  
 (A) Reduction of acyl halide through  $\text{Na}/\text{C}_2\text{H}_5\text{OH}$   
 (B) Reduction of ester through  $\text{Na}/\text{C}_2\text{H}_5\text{OH}$   
 (C) Reduction of anhydride through  $\text{Na}/\text{C}_2\text{H}_5\text{OH}$   
 (D) Reduction of carbonyl compounds through  $\text{Na}/\text{C}_2\text{H}_5\text{OH}$
- Q.2** In which of the following reaction alcohol is not formed-  
 (A)  $\text{R}-\text{CH}=\text{CH}_2 + \text{H}_2\text{O} \xrightarrow[\text{High pr.}]{\text{H}^+}$  (B)  $\text{R}-\text{COCl} + 2\text{H}_2 \xrightarrow{\text{LiAlH}_4}$   
 (C)  $(\text{R}-\text{CO})_2\text{O} + 4\text{H}_2 \xrightarrow{\text{LiAlH}_4}$  (D)  $\text{R}-\text{CH}_2-\text{CH}_3 + \text{H}_2\text{O} \xrightarrow[\text{High pr.}]{\text{H}^+}$
- 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.  $\text{H}_2\text{SO}_4$  (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)<sub>3</sub> solution (B) Ba (OH)<sub>2</sub> solution  
 (C) Ca (OH)<sub>2</sub> 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

|            |     |            |     |            |     |             |     |             |     |            |     |
|------------|-----|------------|-----|------------|-----|-------------|-----|-------------|-----|------------|-----|
| <b>Q.1</b> | (D) | <b>Q.2</b> | (D) | <b>Q.3</b> | (C) | <b>Q.4</b>  | (C) | <b>Q.5</b>  | (B) | <b>Q.6</b> | (B) |
| <b>Q.7</b> | (C) | <b>Q.8</b> | (A) | <b>Q.9</b> | (C) | <b>Q.10</b> | (B) | <b>Q.11</b> | (B) |            |     |

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# ALCOHOL

**(GMP)**

(1) Alkene  $\xrightarrow{\text{H}_2\text{O}}$

(2) RX  $\xrightarrow{\text{aq. NaOH or aq. KOH}}$   
or  $\text{aq. K}_2\text{CO}_3$  or moist  $\text{Ag}_2\text{O}$

(3) R - O - R  $\xrightarrow{\text{dil. H}_2\text{SO}_4}$

(4) RCOOR  $\xrightarrow{\text{dil. H}_2\text{SO}_4}$   
 $\rightarrow \text{RCOOH}$

(5) 1° amine  $\xrightarrow{\text{HNO}_2}$

**Exception - (Methyl amine gives  $\text{CH}_3\text{-O-CH}_3$  or ether)**

(6) Aldehyde or ketone  $\xrightarrow{\text{NaH}}$   
(1° alc.) (2° alc.) Darzens reduction

(7) Acid or  $\xrightarrow{\text{Na/EtOH}}$   
Acid derivative Bouveault-Blanc reduction

(8) HCHO or Ald. or ketone  $\xrightarrow{\text{R-MgX}}$   
(1° alc) (2° alc) (3° alc.)  $\xrightarrow{\text{H}_2\text{O}}$

(9) RMgX  $\xrightarrow{\text{O}_2}$   
 $\xrightarrow{\text{H}_2\text{O}}$

(10)  $\text{CH}_3\text{MgBr}$   $\xrightarrow{\text{CH}_2\text{-CH}_2}$   
 $\xrightarrow{\text{H}_3\text{O}^+}$

(11) Sugar  $\xrightarrow{\text{Fermentation}}$

**(GR)**

(1)  $\xrightarrow{\text{HX or PX}_3 \text{ or } \text{PX}_5}$  or  $\text{KI} + \text{H}_3\text{PO}_4$  or  $\text{SOCl}_2$  or  $\text{SO}_2\text{Cl}_2$   $\rightarrow \text{RX}$

(2)  $\xrightarrow{\text{Red P/HI}}$   $\rightarrow \text{RH}$

(3)  $\xrightarrow{\text{NH}_3}$  1°, 2°, 3° amines

(4)  $\xrightarrow{\text{H}_2\text{S}}$   $\xrightarrow{\text{ThO}_2}$   $\rightarrow \text{R-SH Thiol}$

(5)  $\xrightarrow{\text{Na}}$   $\rightarrow \text{RONa}$

(6)  $\xrightarrow{\text{CH}_3\text{MgX}}$   $\rightarrow \text{CH}_4$

(7)  $\xrightarrow{\text{ald R'-CHO}}$   $\xrightarrow{\text{dry HCl}}$

$\begin{array}{c} \text{R'} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{H} \end{array} \begin{array}{c} \diagup \\ \text{OR} \\ \diagdown \\ \text{OR} \end{array}$

Acetal

(8)  $\xrightarrow{\text{Ketone R'COR'}}$   $\xrightarrow{\text{dry HCl}}$

$\begin{array}{c} \text{R'} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{R'} \end{array} \begin{array}{c} \diagup \\ \text{OR} \\ \diagdown \\ \text{OR} \end{array}$

Ketal

(9)  $\xrightarrow{\text{R'COZ}}$   $\rightarrow \text{R'COOR ester (Z = OH, Cl, OCOCH}_3\text{)}$

(10)  $\xrightarrow{\text{H}_2\text{SO}_4}$   $\rightarrow \text{ROSO}_2\text{OH (Alkyl hydrogen sulphate)}$

(11)  $\xrightarrow{\text{HNO}_3}$   $\rightarrow \text{RONO}_2$  (Alkyl nitrate)

(12)  $\xrightarrow{\text{PhSO}_2\text{Cl}}$   $\rightarrow \text{RSO}_2\text{Ph (Alkyl benzene sulphonate)}$

(13)  $\xrightarrow{\text{CH=CH}}$   $\rightarrow \text{H}_3\text{C-CH (OR)}_2$  Acetal

(14)  $\xrightarrow{\text{CH}_3\text{N}_2}$   $\rightarrow \text{R-O-CH}_3$  Ether

(15)  $\xrightarrow{\text{CH}_2\text{-CH}_2}$   $\rightarrow \text{RO-CH}_2\text{-CH}_2\text{-OH}$   
Alkoxyalkanol

(16)  $\xrightarrow{\text{CH}_2\text{-C=O}}$   $\rightarrow \text{ROCOCH}_3$  Ester

(17)  $\xrightarrow{\text{Dehydration}}$   $\rightarrow \text{Alkene}$

(18)  $\xrightarrow{\text{Catalytic dehydrogenation}}$   $\rightarrow \text{Aldehyde or ketone}$   
1° or 2° alcohol, Cu or ZnO, 300° C  
**Exception - 3° alc  $\rightarrow$  Alkene**

(19) 1° alc.  $\xrightarrow{[\text{O}]}$  Aldehyde  $\xrightarrow{[\text{O}]}$  Acid (same no. of C-atom)

(20) 1° or 2° alc.  $\xrightarrow{\text{O, HCrO}_4^-}$  (orange)  $\rightarrow \text{Aldehyde or ketone} + \text{Cr}^{+3}$  (green)

(21) 3° alc  $\xrightarrow{\text{O, HCrO}_4^-}$  (orange)  $\rightarrow \text{No reaction (No. green colour)}$

**Formation of EtOH by fermentation -**

(1) Cane sugar  $\xrightarrow[\text{Sucrose}]{\text{Crystallization}}$  Molasses

$\xrightarrow[\text{hydrolysis}]{\text{Invertase}}$  Invert sugar  $\xrightarrow[\text{Fermentation}]{\text{zymase}}$  EtOH

(2) Grain  $\rightarrow$  Starch  $\xrightarrow[\text{HOH}]{\text{Diastase}}$  Maltose

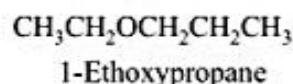
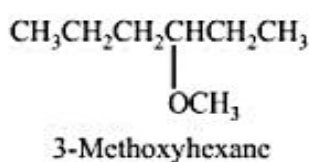
$\xrightarrow[\text{hydrolysis}]{\text{Maltase}}$  Glucose  $\xrightarrow[\text{Fermentation}]{\text{Zymase}}$  EtOH



## ETHERS

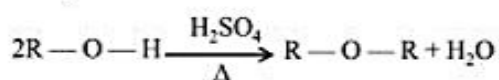
### INTRODUCTION

- (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  $110^\circ$  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  $1.42 \text{ \AA}$ .
- (f) Ether shows chain, position metamerism and functional isomerism. Ethers are functional isomers of alcohols.
- (g) In IUPAC system ethers are called as 'Alkoxy 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.



### PREPARATION

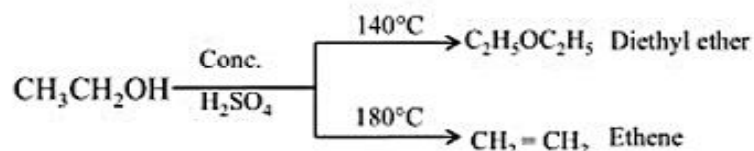
#### 1. Dehydration of alcohols



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.

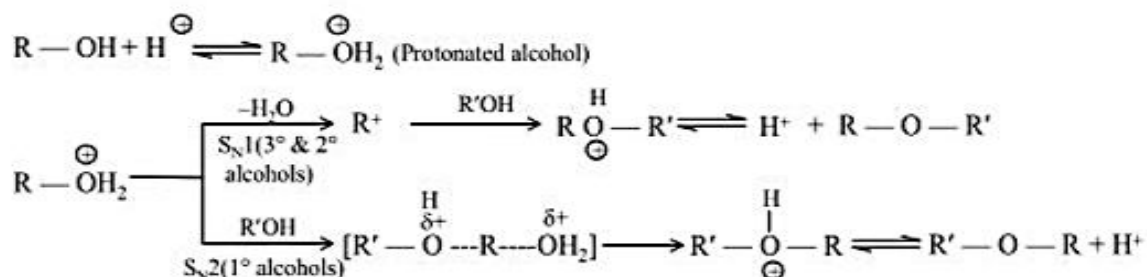
Alcohols can also dehydrate to alkenes, but dehydration to ethers is controlled by the choice of reaction conditions.

Example:

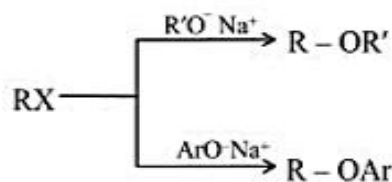


Ether formation by dehydration is an example of nucleophilic substitution: protonated alcohol is the substrate and the second molecule of alcohol is the nucleophile.

The reaction is  $S_N^1$  for  $2^\circ$  and  $3^\circ$  alcohols and  $S_N^2$  for  $1^\circ$  alcohol.

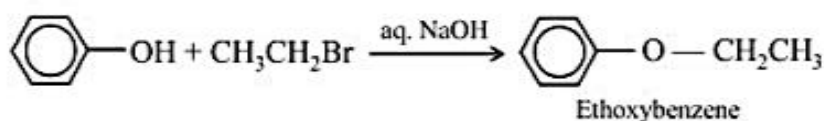
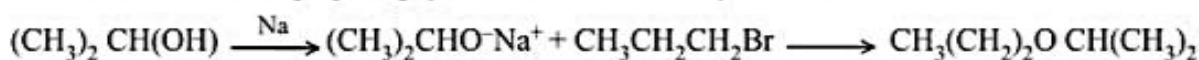


## 2. Williamson synthesis

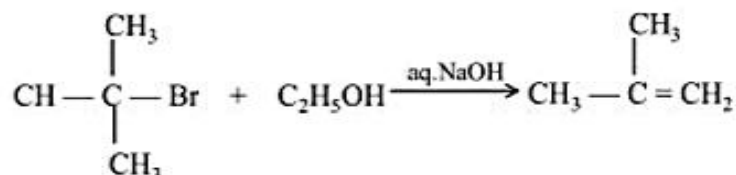


Yield from RX:  $\text{CH}_3 > 1^\circ > 2^\circ > 3^\circ$

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.

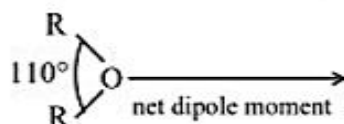


The reaction gives the best yield with  $1^\circ$  alkyl halides. With tertiary alkyl halides, elimination becomes an important reaction and no ether is obtained.

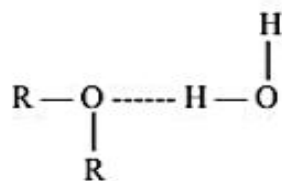


## PHYSICAL PROPERTIES

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



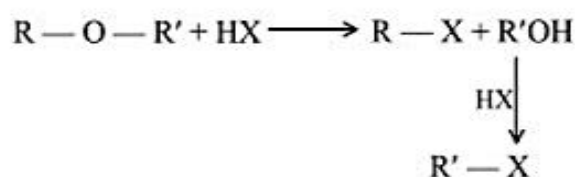
- The boiling point of ethers are the same as those of alkanes of comparable molecular weights. The boiling points of alcohols are much higher than those of ethers, as ethers are incapable for intermolecular hydrogen bonding.
- The solubility of ethers in water is comparable to that of alcohols, because 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.

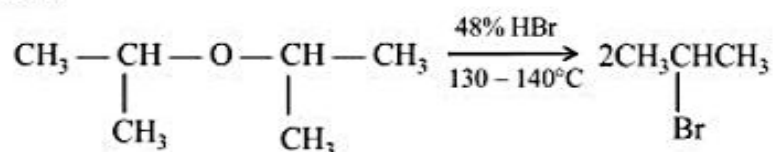
### 1. Cleavage by acids



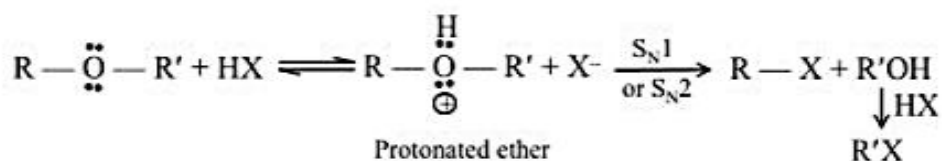
Reactivity of HX :  $\text{HI} > \text{HBr} > \text{HCl}$ .

Cleavage takes place under vigorous conditions using concentrated acids and high temperature.

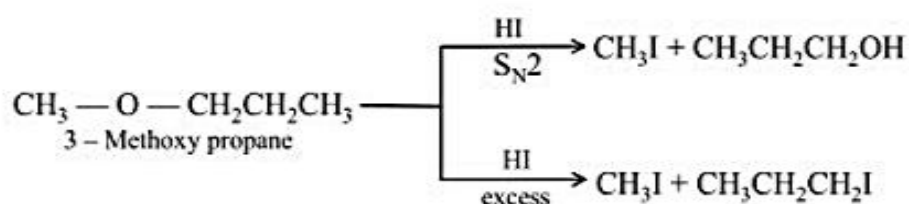
A dialkyl ether initially yields an alkyl halide and an alcohol; the alcohol may further react to form second mole of alkyl halide.

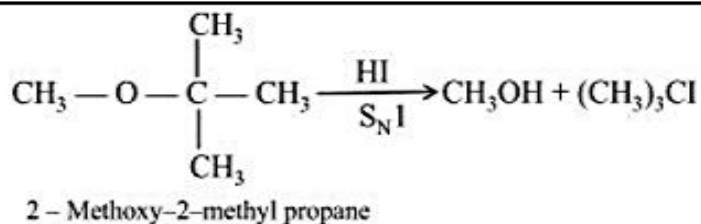


The initial reaction between an ether and an acid results in the formation of a protonated ether. The cleavage then involves a nucleophilic attack by a halide ion on this protonated ether with the displacement of the weakly basic alcohol molecule.



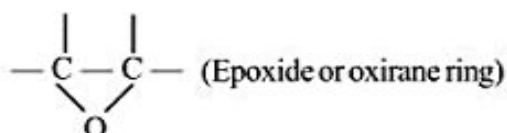
A primary alkyl group tends to undergo  $\text{S}_{\text{N}}2$  displacement and a tertiary alkyl group tends to undergo  $\text{S}_{\text{N}}1$  displacement.



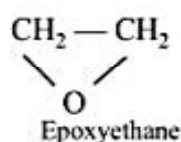
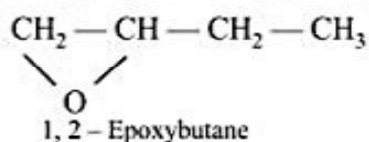


## Epoxides

Epoxides are compounds containing the three-membered ring.

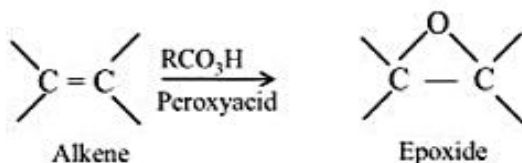


Epoxides belong to a class of compounds called cyclic ethers. The three-membered ring makes epoxides an exceedingly important class of compounds.

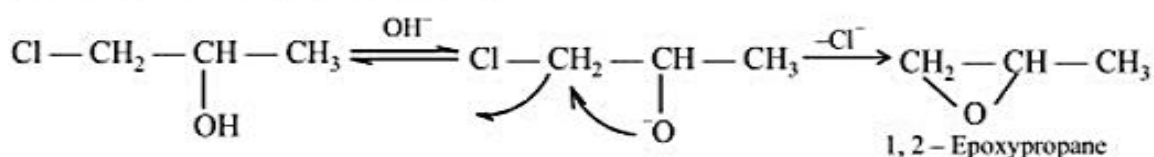


## PREPARATION

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

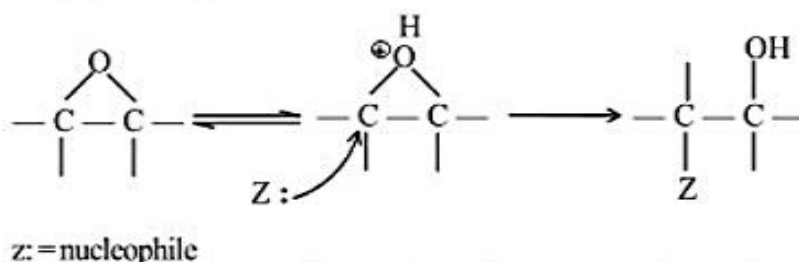


Silver oxide can also oxidise alkenes to epoxides. An internal  $\text{S}_{\text{N}}2$  reaction in a chlorohydrin can be used to prepare three membered cyclic ethers.



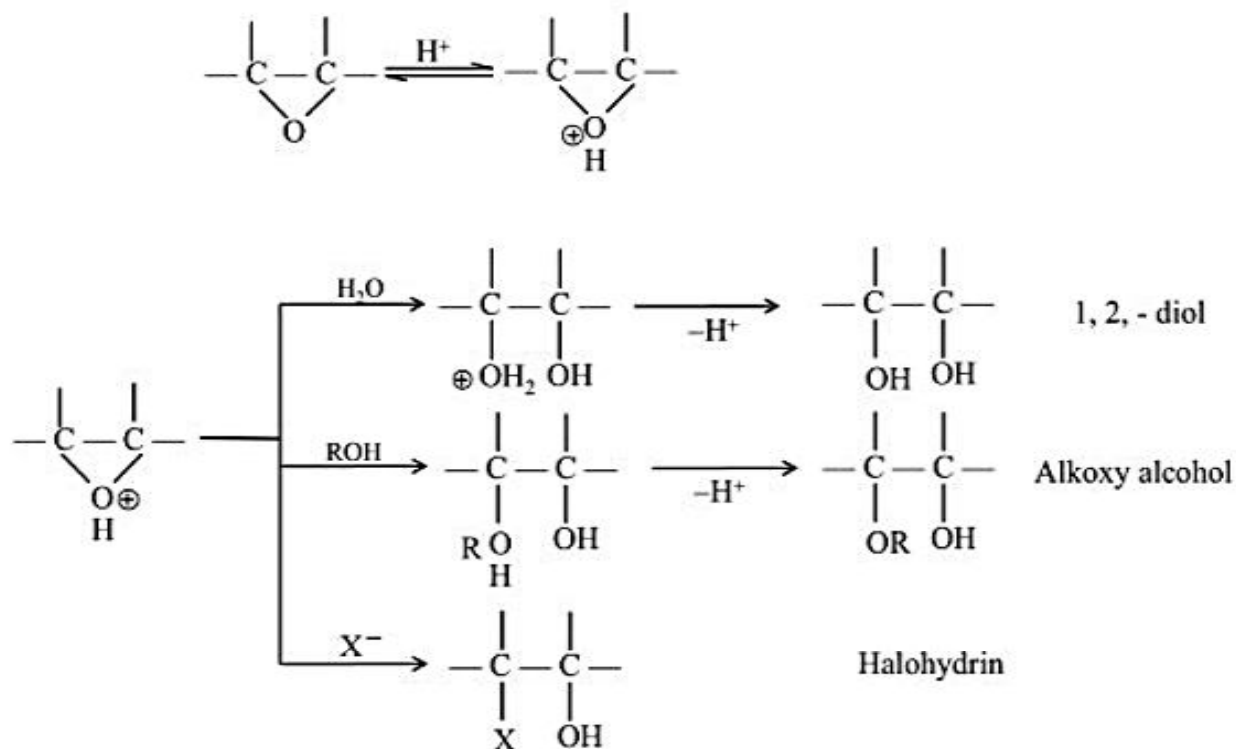
**Reactions :** Epoxides have highly strained three-membered rings that can undergo acid- or base-catalysed ring cleavage.

### 1. Acid-catalysed cleavage

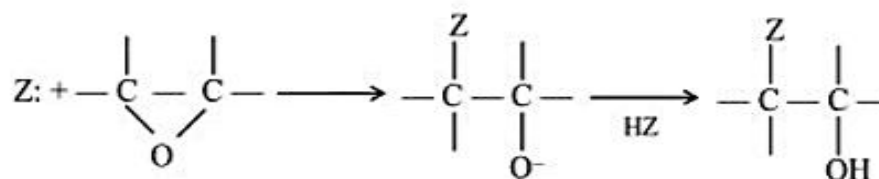


At first, the epoxide is protonated by an acid and the protonated epoxide can then undergo an attack by nucleophilic reagents.

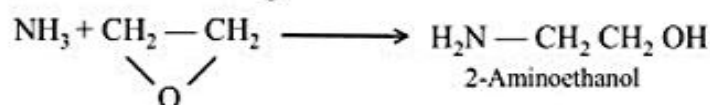
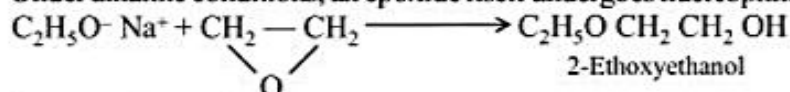




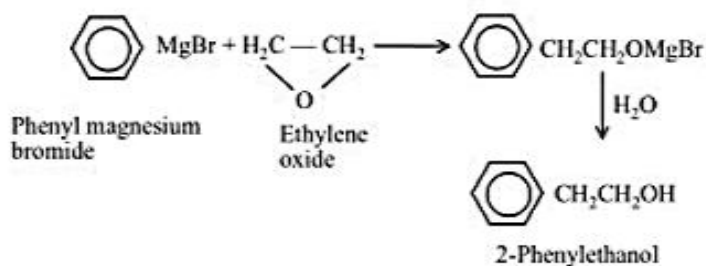
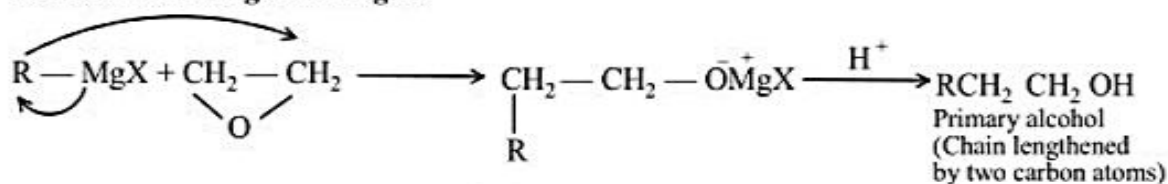
## 2. Base-catalysed cleavage



Under alkaline conditions, an epoxide itself undergoes nucleophilic attack.



## 3. Reaction with Grignard reagent



## MCQ

- Q.1** Ethyl iodide reacts with moist  $\text{Ag}_2\text{O}$  to form –  
 (A) Ether (B) Alcohol (C) Alkene (D) Alkane
- Q.2** Ethyl iodide reacts with sodium ethoxide to form –  
 (A) Ethene (B) Ethoxy ethane (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  $\text{PCl}_5$  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.  $\text{H}_2\text{SO}_4$ , A gives diethyl ether. So A and B are -  
 (A)  $\text{C}_3\text{H}_7\text{OH}$  and  $\text{CH}_3\text{ONa}$  (B)  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{ONa}$   
 (C)  $\text{C}_4\text{H}_9\text{OH}$  and  $\text{C}_4\text{H}_9\text{ONa}$  (D)  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{C}_2\text{H}_5\text{ONa}$
- 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  $\text{PCl}_5$ , but B and C form diethyl ether. Therefore A, and B and C are -  
 (A)  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_2\text{H}_5\text{ONa}$ ,  $\text{C}_2\text{H}_5\text{Cl}$  (B)  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{C}_2\text{H}_5\text{ONa}$ ,  $\text{C}_2\text{H}_5\text{OH}$   
 (C)  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_5\text{Cl}_2$  (D)  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{C}_2\text{H}_5\text{ONa}$
- Q.9** When ethyl iodide is treated with dry silver oxide, it forms -  
 (A) Ag (B)  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  (C)  $\text{C}_2\text{H}_5\text{OH}$  (D)  $\text{COOH} - \text{COOH}$
- Q.10** C—O—C bond angle in diethyl ether is about-  
 (A)  $180^\circ$  (B)  $110^\circ$  (C)  $150^\circ$  (D)  $90^\circ$

## 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 (C<sub>6</sub>H<sub>5</sub>OH)

Phenol is also known as carbolic acid or Benzenol or hydroxy benzene.

In phenol –OH group is attached to sp<sup>2</sup> – hybridised carbon.

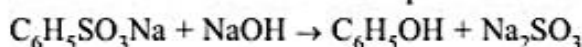
It was discovered by Runge in the middle oil fraction of coaltar distillation and named it carbolic acid (carbo = coal; oleum = oil)

It is also present in traces of human urine.

### METHODS OF PREPARATION

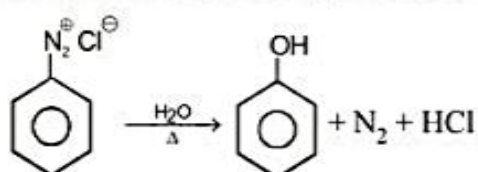
**[1] From Benzene sulphonic acid :**

When sodium salt of benzene sulphonic acid is fused with NaOH phenol is obtained.

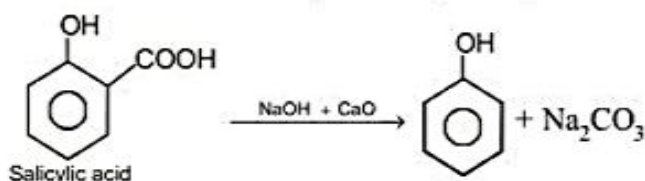


**[2] From benzene diazonium chloride :**

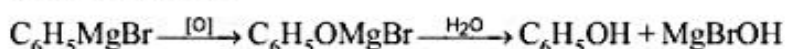
When benzene diazonium chloride solution is warmed phenol is obtained with evolution of nitrogen.



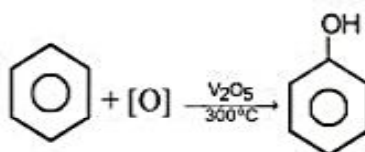
**[3] By distilling a phenolic acid : with sodalime (decarboxylation) :**



**[4] From Grignard reagent :** The grignard reagent on reaction with oxygen and subsequent hydrolysis by acid yields phenol

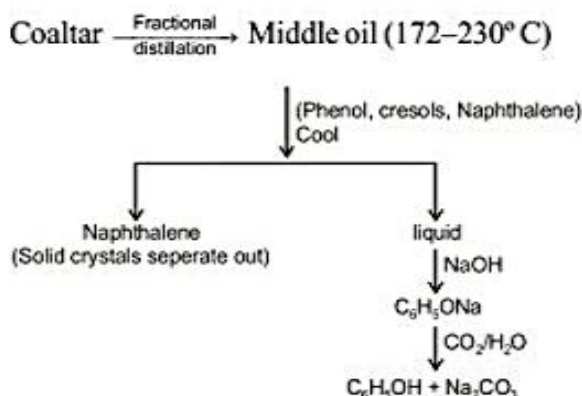
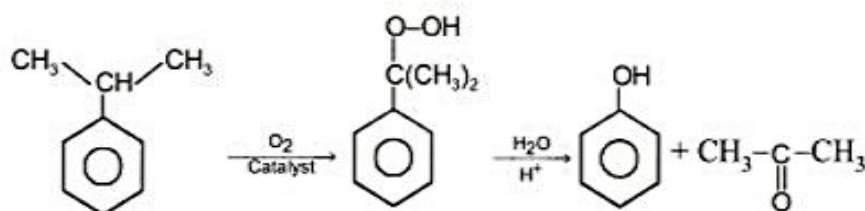
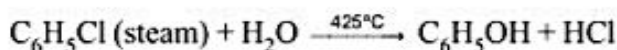
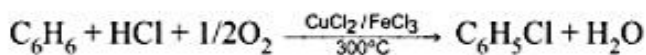
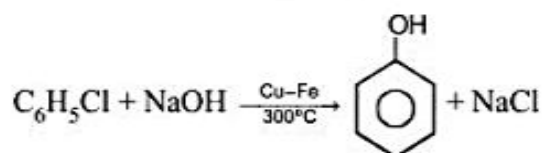


**[5] From benzene :**

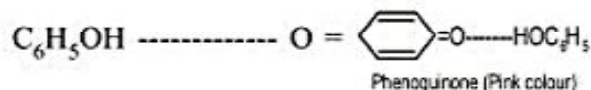


**[6] Industrial preparation of phenol :** Phenol can be prepared commercially by :

- [a] Middle oil fraction of coaltar distillation
- [b] Raschig process
- [c] Dow's process
- [d] Cumene

**[a] Middle oil fraction of coaltar :****[b] From cumene : (Isopropyl benzene) :** Cumene is oxidised with oxygen in to cumene hydro peroxide in presence of a catalyst. This is decomposed by dil.  $\text{H}_2\text{SO}_4$  in to phenol and acetone.**[c] Raschig process :** Chlorobenzene is formed by the interaction of benzene  $\text{HCl}$  and air at 300°C in presence of catalyst  $\text{CuCl}_2 + \text{FeCl}_3$ . It is hydrolysed by superheated steam at 425°C to form phenol and  $\text{HCl}$ .**[d] Dow process :** This process involves alkaline hydrolysis of chloro benzene**PHYSICAL PROPERTIES**

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



- 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 phenoxide ion in solution.

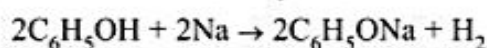


The phenoxide ion is stable due to resonance.

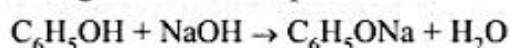
- The negative charge is spread through out the benzene ring which is stabilising factor in the phenoxide ion.
- Electron withdrawing groups ( $-\text{NO}_2$ ,  $-\text{Cl}$ ) increase the acidity of phenol while electron releasing groups ( $-\text{CH}_3$  etc.) decrease the acidity of phenol.
- Phenol 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 electropositive metals react with phenol.



[iii] Phenol reacts with strong alkalis to form phenoxides

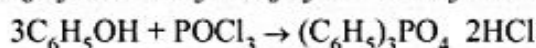
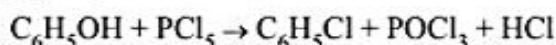


[vi] However phenol does not decompose  $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$  because phenol is weaker acid than carbonic acid.

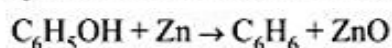


### Reaction due to —OH group :

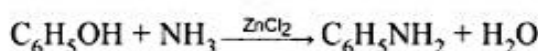
[1] **Reaction with  $\text{PCl}_5$  :** Phenol reacts with  $\text{PCl}_5$  to form chloro benzene. The yield of chlorobenzene is poor and mainly triphenyl phosphate is formed.



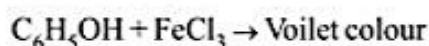
[2] **Reaction with Zn dust :** When phenol is distilled with zinc dust benzene is obtained.



[3] **Reaction with  $\text{NH}_3$  :** Phenol reacts with  $\text{NH}_3$  in presence of anhydrous  $\text{ZnCl}_2$  to form aniline.

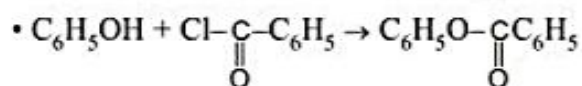
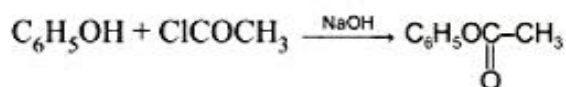


[4] **Reaction with  $\text{FeCl}_3$  :** Phenol gives violet colouration with  $\text{FeCl}_3$  solution (neutral) due to formation of a complex.



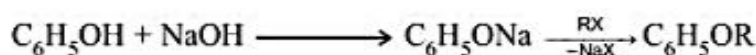
- This reaction is used to differentiate phenol from alcohols.

- [5] **Acetylation** : Phenol reacts with acid chlorides or acid anhydrides in alkali solution to form phenyl esters.



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

- [6] **Ether Formation** : Phenol reacts with alkyl halides in alkali solution to form phenyl ethers.

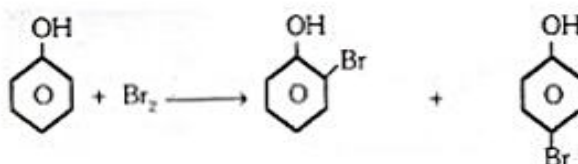


- [7] **Reaction with  $\text{P}_2\text{S}_5$**  :

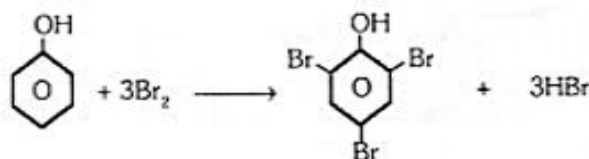


**Reaction of Benzene Ring** : The  $-\text{OH}$  group is ortho and para directing. It activates the benzene nucleus.

- [1] **Halogenation** : Phenol reacts with bromine in  $\text{CCl}_4$  to form mixture of o- and p-bromo phenol.

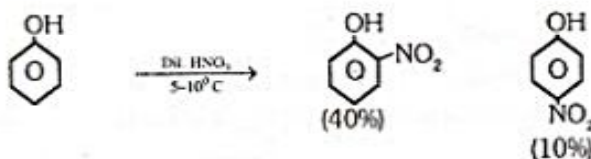


- Phenol reacts with bromine water to form a white ppt. of 2, 4, 6 tribromo phenol.

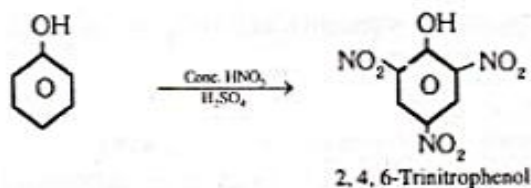


- [2] **Nitration** :

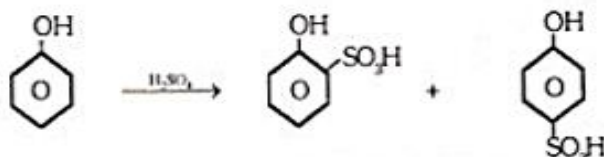
[a] Phenol reacts with dil.  $\text{HNO}_3$  at  $5-10^\circ\text{C}$  to form o- and p- nitro phenols.



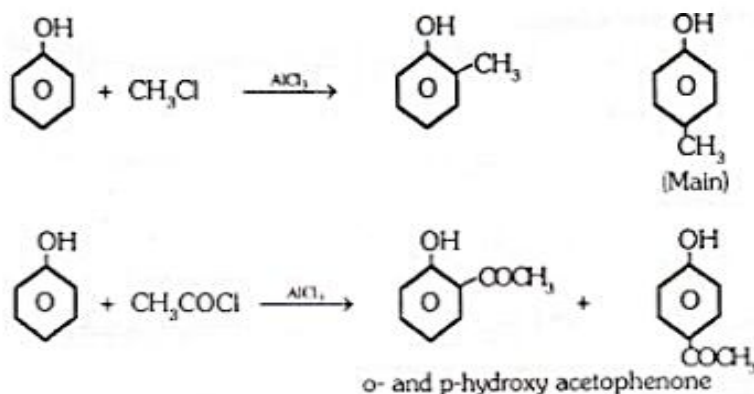
[b] When phenol is treated with conc.  $\text{HNO}_3$  in presence of conc.  $\text{H}_2\text{SO}_4$  2,4,6-trinitro phenol (picric acid) is formed.



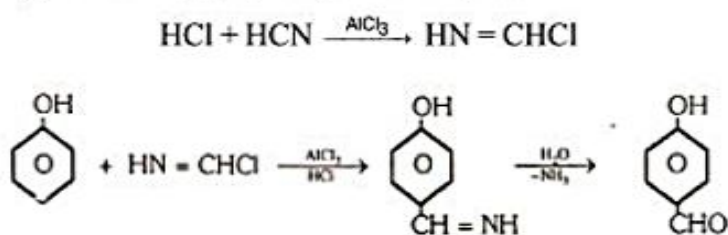
- [3] **Sulphonation** : Phenol reacts with conc.  $\text{H}_2\text{SO}_4$  to form mixture of o- and p-hydroxy benzene sulphonic acid.



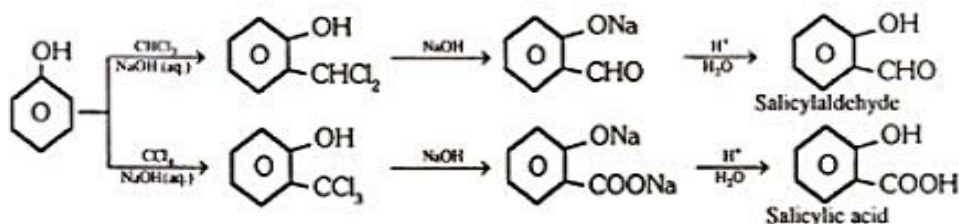
- [4] **Friedel–Craft’s reaction** : Phenol when treated with methyl chloride in presence of anhydrous  $\text{AlCl}_3$  p-cresol is main product.



- [5] **Gattermann aldehyde synthesis** : When phenol is treated with liquid HCN and HCl gas in presence of anhydrous  $\text{AlCl}_3$  yields mainly p-hydroxy benzaldehyde.

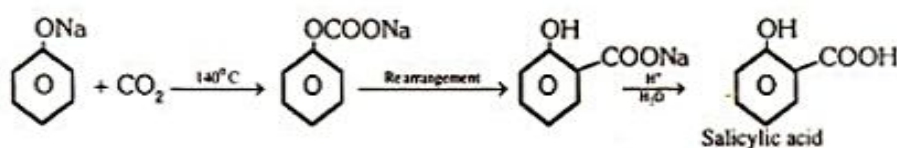


- [6] **Reimer–Tiemann reaction** : Phenol on refluxing with chloroform and NaOH (aqueous) followed by acid hydrolysis yields o-hydroxy benzaldehyde. When  $\text{CCl}_4$  is used salicylic acid is formed.

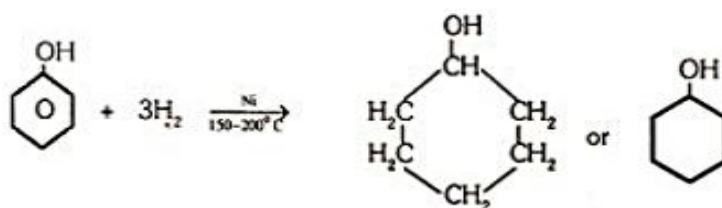




- [7] **Kolbe's Schmidt reaction :** This involves the reaction of  $\text{C}_6\text{H}_5\text{ONa}$  with  $\text{CO}_2$  at  $140^\circ\text{C}$  followed by acid hydrolysis salicylic acid is formed.

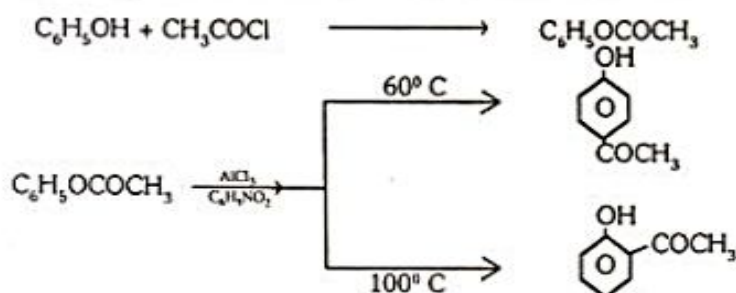


- [8] **Hydrogenation :** Phenol when hydrogenated in presence of Ni at  $150\text{--}200^\circ\text{C}$  forms cyclohexanol.

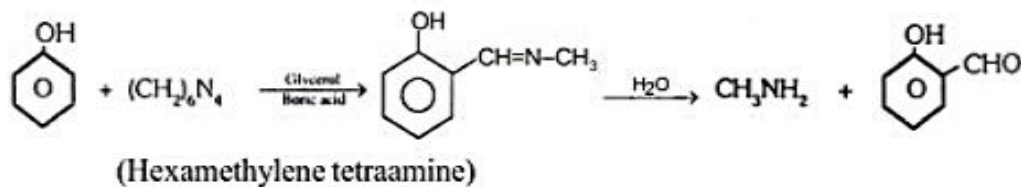


- [9] **Fries rearrangement reaction :**

When phenyl ester is heated in nitrobenzene solution, in the presence of anhyd.  $\text{AlCl}_3$  then rearrangement takes place in which acyl group is transferred at o - & p-positions of phenolic group. Up to  $60^\circ\text{C}$ , para product is obtained mainly and above  $160^\circ\text{C}$  ortho products are obtained as major product.

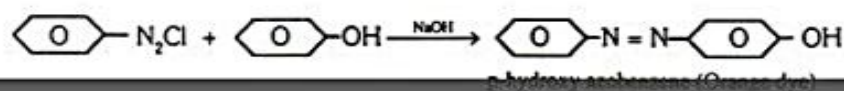


- [10] **Duff's reaction :**



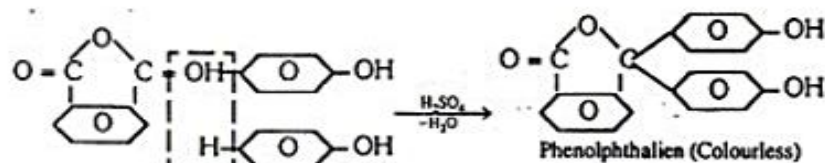
- [11] **Coupling reactions :**

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

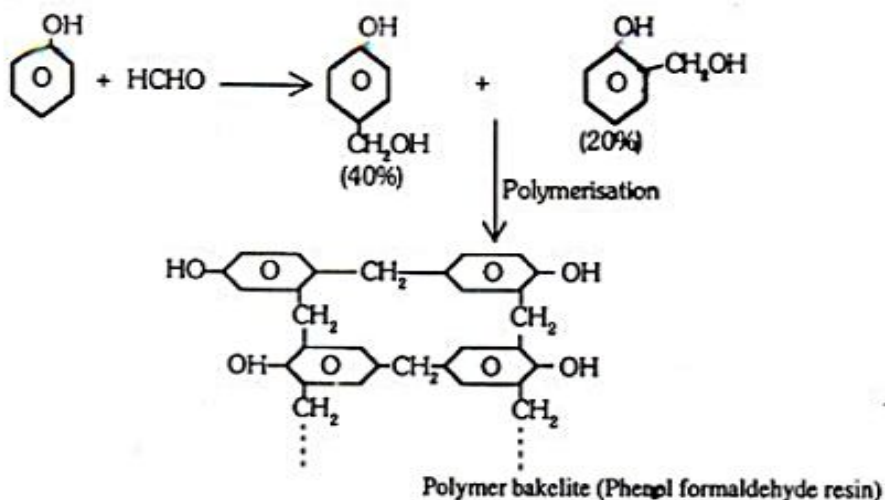




- [b] Phenol couples with phthalic anhydride in presence of conc.  $\text{H}_2\text{SO}_4$  to form a dye (phenolphthalien)

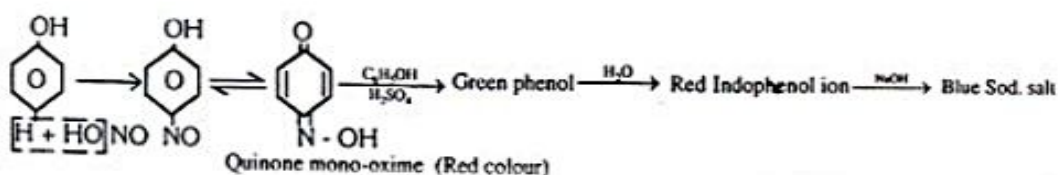


- [12] **Condensation with formaldehyde :** Phenol condenses with  $\text{HCHO}$  (excess) in presence of  $\text{NaOH}$  to form a polymer known as bakelite.

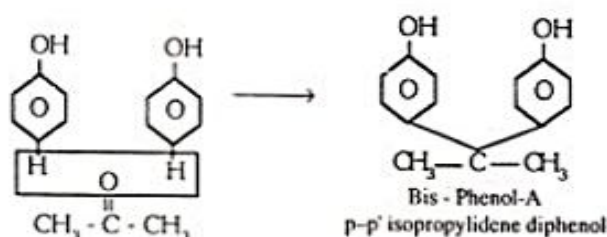


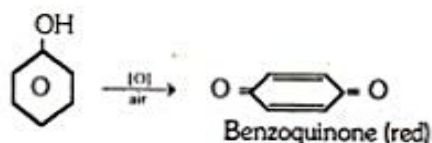
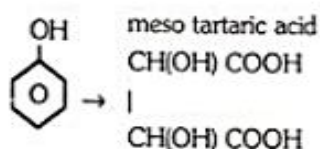
- [13] **Liberman's nitroso reaction :** When phenol is reacted with  $\text{NaNO}_2$  and conc.  $\text{H}_2\text{SO}_4$  it gives a deep green or blue colour which changes to red on dilution with water. When made alkaline with  $\text{NaOH}$  original green or blue colour is restored.

The reaction is used as a test of phenol.

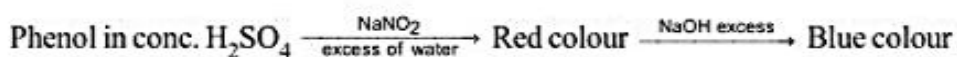


- [14] **Reaction with acetone :**



**[15] Oxidation :****[1] In presence of air :****[2]  $\text{KMnO}_4$  :****Test of Phenol :**

- [1] Phenol turns blue litmus to red.
- [2] Aqueous solution of phenol gives a violet colour with a drop of ferric chloride.
- [3] Phenol gives Lieber mann's nitroso test.



- [4] Aqueous solution of phenol gives a white ppt. of 2,4,6 tribromophenol with bromine water.
- [5] Phenol combines with phthalic anhydride in presence of conc.  $\text{H}_2\text{SO}_4$  to form phenolphthalein which gives pink colour with alkali.
- [6] With ammonia and sodium hypochlorite, phenol gives blue colour.

**Differences between phenol and alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) :**

- [1] Phenol is more acidic than aliphatic alcohol due to resonance in phenoxide ion.
- [2] Phenol gives violet colour with  $\text{FeCl}_3$  while aliphatic alcohol does not give.
- [3] Phenol gives triphenyl phosphate with  $\text{PCl}_5$  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.
- [4] As preservation for ink.

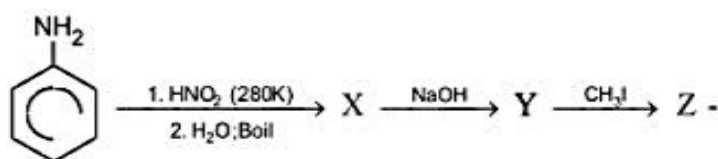
| S.No. | Test/Reaction            | Alcohol     | Phenol                   |
|-------|--------------------------|-------------|--------------------------|
| 1.    | Litmus test              | No Reaction | Blue litmus red          |
| 2.    | $\text{FeCl}_3$ Solution | No Reaction | Violet colour            |
| 3.    | Benzene diazonium salt   | No Reaction | Yellow or orange azo dye |
| 4.    | $\text{Br}_2$ water      | No Reaction | 2, 4, 6-tribromophenol   |

### 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 -



- (A)
- (B)
- (C)
- (D)

**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

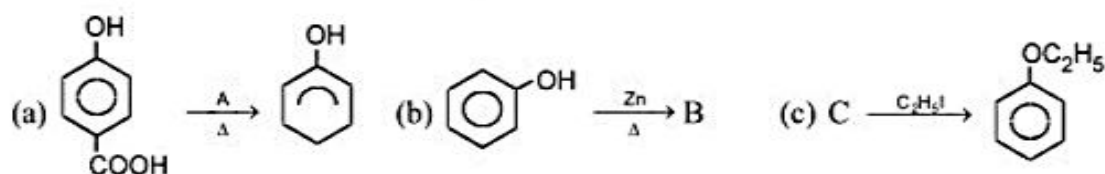
**Q.4** Which among the following is the strongest o-, p-directing group in benzene is -

- (A) —OH (B) —Cl (C) —OCH<sub>3</sub> (D) —CH<sub>3</sub>

**Q.5** The compound represented by the molecular formula  $\text{C}_7\text{H}_8\text{O}$  are -

- (A) Only alcohol (B) Only ether  
 (C) Only phenolic compound (D) All the three types of compounds

Q.6 Identify A, B, and C in the following reactions—



- (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  $\phi = C_6H_5$ ]

- (A)  $\phi-COOH$  (B)  $\phi-OH$  (C)  $\phi-CO-CH_3$  (D)  $\phi-NH_2$

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)  $-CHO$  and  $-NO_2$  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

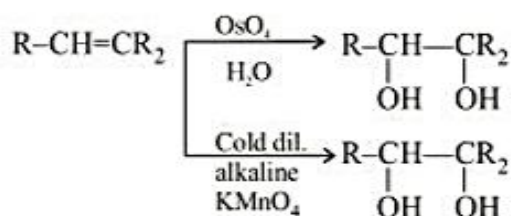
#### ANSWER KEY

- |     |     |     |     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 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) |     |     |



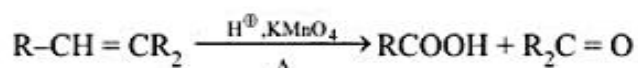
## OXIDATION OF ALKENES, ALCOHOLS & CARBONYL COMPOUNDS

### (I) OXIDATION OF ALKENES



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

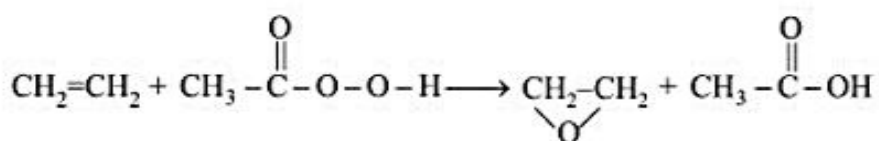
If we use acidic  $\text{KMnO}_4$  or warm  $\text{KMnO}_4$  or too concentrated  $\text{KMnO}_4$  the oxidative cleavage of Glycol occurs resulting in mixture of Carboxylic acids & Ketones.



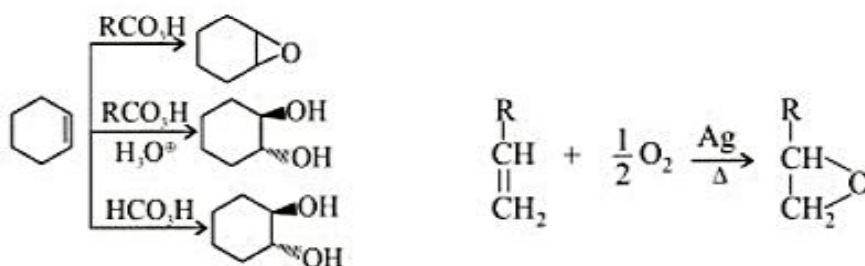
Hot acidic  $\text{KMnO}_4$ , Hot acidic  $\text{K}_2\text{Cr}_2\text{O}_7$  & hot acidic  $\text{NaIO}_4$  gives same result with alkene. The effect is similar to that of oxidative ozonolysis on alkenes.

#### Preilschaive reaction :

Epoxidation of alkenes is reaction of alkenes with peroxyacids.

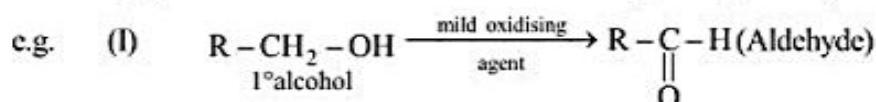


- With the decrease in nucleophilicity of double bond, rate of reaction decreases.
- With the decrease in  $e^-$  withdrawing substituents in leaving group, rate decreases.

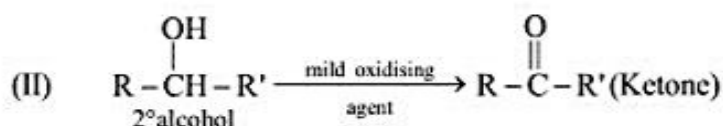




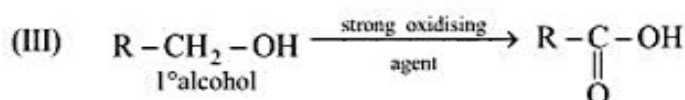
Different oxidising agents are used to oxidise alcohols in corresponding carbonyl compounds and carboxylic acids.



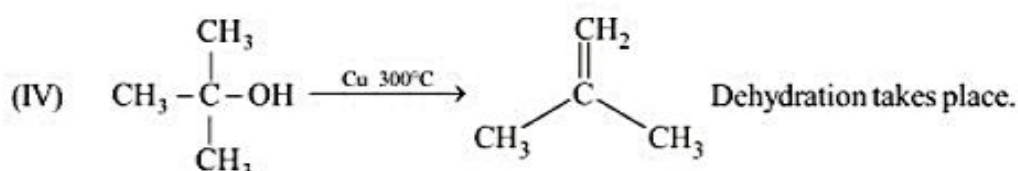
Oxidation agent : 1,4,5,6,7,8,9,12



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



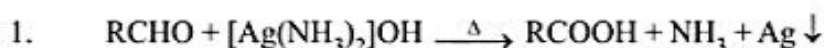
Oxidation agent : 2,3



(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



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

2. **Fehling's Solutions**

Fehling's A

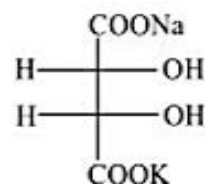
aq.  $\text{CuSO}_4$

Fehling's B

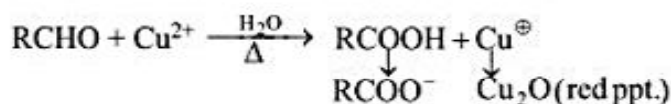
Alk. solution of Roschelye

salt (sodium potassium tartrate)

It acts a carrier for  $\text{Cu}^{2+}$  as it make reversible complex with  $\text{Cu}^{2+}$

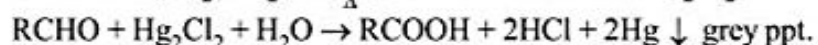
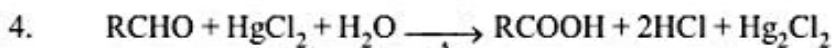
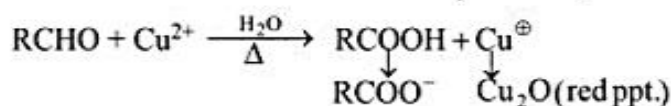


This test is also used is Blood and Urine test.



3. **Benedict's solution**

Sodium Citrate + NaOH +  $\text{NaHCO}_3$  +  $\text{CuSO}_4$

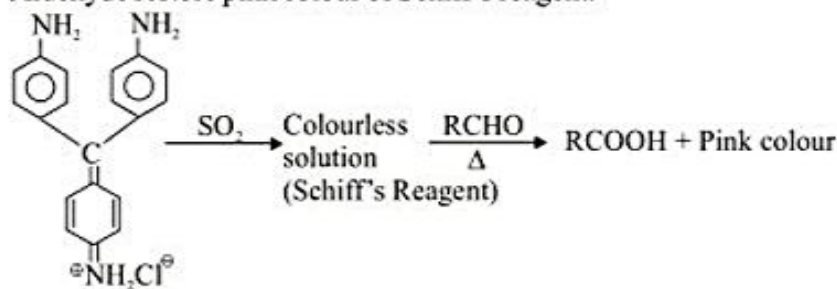




### 5. Schiff's Reagent

Schiff's Reagent is aq. solution of following base decolourised by passing  $\text{SO}_2$ .

Aldehyde restore pink colour of Schiff's reagent.



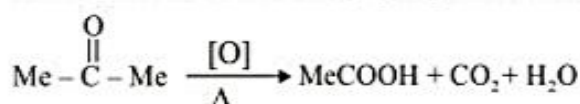
p-Rosaniline Hydrochloride

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

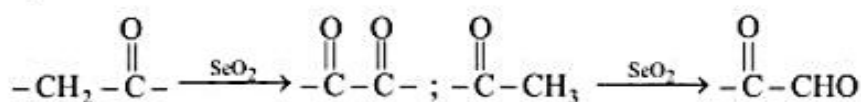
## KETONES ARE DIFFICULT TO OXIDIZE

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.

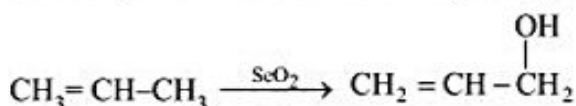


### Allylic oxidation

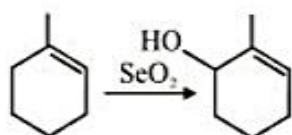
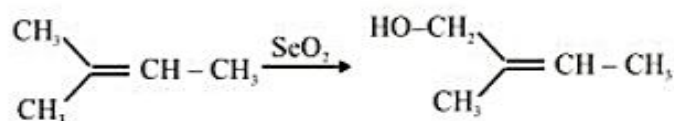
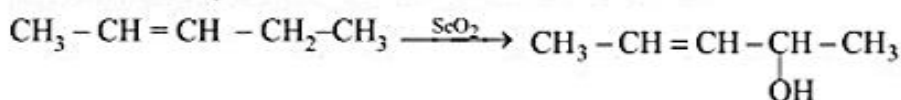
$\text{SeO}_2$  is a selective oxidizing agent with converts  $-\text{CH}_2-$  group adjacent to carbonyl group into carbonyl group. The reagent, in general, oxidises active methylene and methyl groups to ketonic and aldehydic groups respectively.



Double bonds, triple bonds and aromatic rings may also activate the methylene group. The methylene or methyl group  $\alpha$  to the most highly substituted end of the double bond is hydroxylated according to the order of preference of oxidation  $\text{CH}_2 > \text{CH}_3 > \text{CH}$  groups.



Rate of reactivity order  $2^\circ \text{C} - \text{H} > 1^\circ \text{C} - \text{H} > 3^\circ \text{C} - \text{H}$





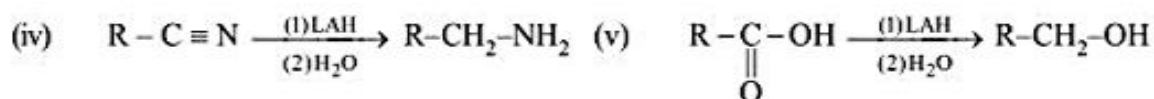
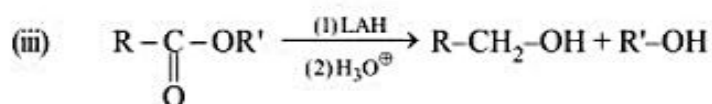
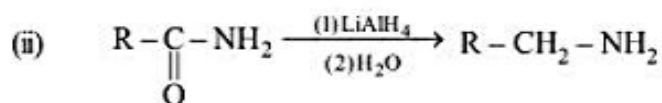
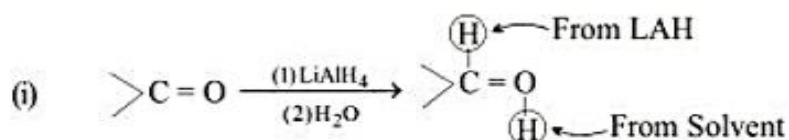
### Reducing agents and their role

| Group                | Product                          | LAH in ether | LiAlH(OCMe <sub>3</sub> ) <sub>3</sub> in THF | NaBH <sub>4</sub> in EtOH | H <sub>2</sub> <sup>+</sup> ** catalyst |
|----------------------|----------------------------------|--------------|---|---------------------------|---|
| -CHO                 | -CH <sub>2</sub> OH              | +            | -   | +                         | +                                       |
| >C=O                 | >CH-OH                           | +            | -   | +                         | +                                       |
| -CO <sub>2</sub> H   | -CH <sub>2</sub> OH              | +            | -   | -                         | +                                       |
| -CO <sub>2</sub> R   | -CH <sub>2</sub> OH              | +            | -   | -                         | +                                       |
| -COCl                | -CH <sub>2</sub> OH              | +            | +   | +                         | +                                       |
| -CONH <sub>2</sub>   | -CH <sub>2</sub> NH <sub>2</sub> | +            | -   | -                         | +                                       |
| (RCO) <sub>2</sub> O | RCH <sub>2</sub> OH              | +            | -   | -                         | +                                       |
| -CN                  | -CH <sub>2</sub> NH <sub>2</sub> | +            | -   | -                         | +                                       |
| >C=NOH               | -CH <sub>2</sub> NH <sub>2</sub> | +            | -   | -                         | +                                       |
| >C=C<                | >CH-CH<                          | -            | -   | -                         | +                                       |
| -C≡C-                | -CH=CH-                          | -            | -   | -                         | +                                       |
| 1° RX                | RH                               | +            | -   | -                         | +                                       |

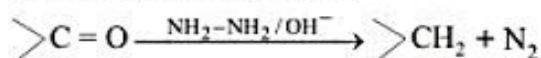
\* Product is RCHO

\*\* Catalyst : Ni / Pd / Pt / Ru

**LiAlH<sub>4</sub> as a reducing agent :**



**Wolf Kischner reduction :**



**Clemenson reduction**

