

# 10

# ALCOHOLS, PHENOLS AND ETHERS

#### HYDROXY DERIVATIVES



- (I) Aliphatic hydroxy derivatives : Hydroxy derivatives in which – OH is directly attached to sp<sup>3</sup> C (Alcoholic compounds).
- (II) Aromatic hydroxy derivatives : Hydroxy derivatives in which – OH is directly attached to sp<sup>2</sup> C or benzene ring (Phenolic compounds).

#### Aliphatic hydroxy derivatives

(a) Classification according to number of -OH groups : (i) Monohydric [one -OH]  $\longrightarrow CH_3CH_2 - OH$ 

(ii) Dihydric [two-OH] 
$$\longrightarrow$$
 CH<sub>2</sub> - CH<sub>2</sub>  
 $|$  | |  
OH OH

(iii) Trihydric [three – OH 
$$\longrightarrow$$
 CH<sub>2</sub> – CH – CH<sub>2</sub>  
| | | |  
OH OH OH

(iv) Polyhydric [n– OH 
$$\longrightarrow$$
 CH<sub>2</sub> – CH-----CH<sub>2</sub>  
 $|$  | | |  
OH OH OH

#### (b) Classification according to nature of carbon :

(i) p or 1° alcohol  $\longrightarrow$  CH<sub>3</sub>CH<sub>2</sub> – OH (ii) s or 2° alcohol  $\longrightarrow$  (CH<sub>3</sub>)<sub>2</sub>CH – OH (iii) t or 3° alcohol  $\longrightarrow$  (CH<sub>3</sub>)<sub>3</sub>C – OH

#### **ALCOHOLS**

Alcohols are bent molecules. The carbon atom (linked with O atom of – OH group) is sp<sup>3</sup> hybridised. The central O atom is also in sp<sup>3</sup> state of hybridisation. The bond angle is 108.5°. In sp<sup>3</sup> hybridisation of O –  $2s^2$ ,  $2p_x^2$ ,  $2p_y^1$ ,  $2p_z^1$  orbitals hybridised to form sp<sup>3</sup> orbitals.

In these four orbitals two containing one electron each and two containing two electrons each. Orbitals containing two electrons do not take part in bonding. Other two half filled orbitals form  $\sigma$  bond with s-orbitals of H-atom and hybridised orbital of C-atom (O – C).

Due to lone pair effect the bond angle of tetrahedral oxygen atom is lesser than normal tetrahedral structure (109°28').

#### METHODS OF PREPARATION

#### From Alkyl halides (hydrolysis) :

Alkyl halides hydrolysed with aq. KOH/moist  $Ag_2O$  or AgOH or  $H_2O$  forms alcohol.

The hydrolysis occurs by a nucleophilic substitution reaction.  $P_{1} C H_{1} X + A z O H (ag) \rightarrow P_{2} C H_{2} O H + A z X$ 

$$R - CH_2 - X + AgOH(aq.) \longrightarrow R - CH_2 - OH + AgX$$

$$1^{\circ} Alcohol$$

$$R \qquad R \qquad | \\ CH - X + K - OH(aq.) \longrightarrow R - CH - OH + KX$$

$$Alkyl halide \qquad 2^{\circ} Alcohol$$

$$\begin{array}{c} R \\ | \\ R - C - X + H - OH \longrightarrow R - C - OH + HX \\ | \\ R \\ R \\ R \\ \end{array}$$

#### 3° Alcohol

#### From Alkenes (Hydration) :

$$\begin{array}{c} \text{R-CH=CH}_{2} + \text{H}_{2}\text{O} \xrightarrow{\text{dil}.\text{H}_{2}\text{SO}_{4}} & \text{R} - \text{CH} - \text{CH}_{3} \\ & & | \\ & & \text{OH} \\ & & \text{OH} \\ & & \text{Alkene} & 2^{\circ} \text{ Alcohol} \end{array}$$

$$CH_2=CH_2+H_2O \xrightarrow{dil.H_2SO_4} CH_3-CH_2-OH$$

Ethene Ethanol

#### By Reduction of Carbonyl compounds :

$$\begin{array}{c} R - C - H + 2H & \xrightarrow{\text{LiAlH}_4/\text{Na} + C_2\text{H}_5\text{OH}/\text{NaH}} & R - C\text{H}_2\text{OH} \\ \\ \parallel & O \\ \\ \text{Aldehyde} & 1^\circ \text{alcohol} \\ R - C - R + 2H & \xrightarrow{\text{LiAlH}_4/\text{Na} + C_2\text{H}_5\text{OH}/\text{NaH}} & R - C\text{H} - R \\ \\ \parallel & & \parallel \end{array}$$

$$\begin{array}{c} || \\ || \\ O \\ Ketone \end{array} \qquad \begin{array}{c} || \\ || \\ O \\ CH \\ 2^{\circ} alcohol \end{array}$$

**Note :** 3° alcohol cannot be obtained by this method **By reduction of Acid & Its derivatives :** 

$$\begin{array}{c} R - C - OH + 4H \xrightarrow{\text{LiAlH}_4} RCH_2OH \\ \parallel \\ O \\ Carboxylic acid \\ Alcohol \end{array}$$

$$\begin{array}{c} R - C - X + 4H \xrightarrow{\text{LiAlH}_4} RCH_2OH + HX \\ \parallel \\ O \\ Acid halide \\ Alcohol \end{array}$$



$$\begin{array}{c} R - C - OR' + 4H \xrightarrow{\text{LiAlH}_4} RCH_2OH + R'OH \\ \parallel \\ O \\ \text{Acid ester} & \text{Alcohol} \end{array}$$

Acid ester

$$\text{RCOOCOR} + 8\text{H} \xrightarrow{\text{LiAlH}_4} 2\text{RCH}_2\text{OH} + \text{H}_2\text{O}$$

Acid anhydride Alcohol

Acid amide on reduction forms primary amine as major product not alcohol.

#### From Grignard reagent :

#### (1) Primary alcohol:

(a) With oxygen : By the action of Grignard reagent on oxygen forms alcohol of same no. of carbon atoms as in Grignard reagent.

$$2R - Mg - X + O_2 \xrightarrow{\Delta} 2R - O - Mg - X$$

$$\xrightarrow{2HOH}$$
 2ROH + 2Mg(X)OH

Primary alcohol

(b) With formaldehyde:

$$R - MgX + \frac{H}{H} C = O \longrightarrow \frac{H}{H} C < R^{OMgX}$$

$$\xrightarrow{H_2O} RCH_2OH + Mg <_X^{OH}$$

The alcohol has one carbon atom more than the alkyl group of grignard reagent

#### (c) With ethylene oxide :

$$R - Mg - X + CH_2 - CH_2 \text{ (Ethylene oxide)}$$

$$\longrightarrow R - CH_2 - CH_2 - O - Mg - X$$

$$\xrightarrow{H_2O} R - CH_2 - CH_2OH + Mg(X)OH$$
Alcohol

The alcohol has two carbon atom more than alkyl group of the Grignard reagent.

2. Secondary and tertiary alcohol: With carbonyl compounds

$$\overset{\delta-}{\operatorname{Mg}} \overset{\delta+}{\operatorname{Mg}} \overset{H}{\operatorname{Mg}} \overset$$

$$\begin{array}{c} \begin{array}{c} H \\ R' \stackrel{I}{\longrightarrow} C \stackrel{R}{\longrightarrow} R \\ \downarrow \\ O \stackrel{Mg}{\longrightarrow} X \end{array} \xrightarrow{H_2O} R' \stackrel{H}{\longrightarrow} C \stackrel{H}{\longrightarrow} R$$

(Secondary alcohol)

- (i) If carbonyl compound is ketone, product will be tertiary alcohol.
- (ii) It is the best method for preparation of alcohol because we can prepare every type of alcohols.

From Primary amines : Primary alcohol are formed when primary amines are treated with nitrous acid (HNO<sub>2</sub>)

$$R - NH_2 + HNO_2 \xrightarrow{HCl} R - OH + N_2 + H_2O$$

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.

Hydrolysis of ether : Ether when heated with dilute sulphuric acid under pressure are hydrolysed to the corresponding alcohols.

$$\begin{array}{c} \text{ROR'+HOH} \xrightarrow{\text{dil.H}_2\text{SO}_4} \text{ROH} + \text{R'OH} \\ \text{Ether} & \text{alcohol} \end{array}$$

#### **PHYSICAL PROPERTIES**

- Alcohols are colourless with characteristic smell (alcoholic) (i) liquid.
- They are soluble in water due to H-bonding. These are (ii) partially soluble in organic solvents.
- (iii) They are liquid in nature up to 12-carbon.
- (iv) Melting point and Boiling point  $\propto$  molecular mass

$$\propto \frac{1}{\text{No. of branches}}$$

(v) Boiling point of alcohols are higher than equivalent ethers. Due to H-bonding.

#### **CHEMICAL PROPERTIES**

- (A) Reactions involving the cleavage of O-H bond : These are the reactions in which alcohol shows acidic character. The general order of reactivity of alcohols in this type of reaction is : Primary > Secondary > Tertiary
- Reaction with metal: On reaction with active metals like -1. Na, K, Ca, Mg, Al, etc liberate hydrogen

$$2R-O-H+2Na \longrightarrow 2R-O-Na+H_2$$
  
Sodium alkoxide

The acidic order of alcohols is : MeOH >  $1^{\circ} > 2^{\circ} > 3^{\circ}$ Reaction with carboxylic acid (Esterification) :

$$\begin{array}{c} \text{R-O-H+H-O-C-R} \xrightarrow[]{\text{conc.H}_2\text{SO}_4} \\ \parallel \\ \text{O} \end{array}$$

alcohol acid

R - 0

$$R - C - O - R^{+} H_{2}O$$

$$Mechanism: H_{2}SO_{4} \longrightarrow H^{+} + HSO_{4}^{-}$$

$$R - C - \stackrel{\oplus}{O} - H^{+} H^{+} \longrightarrow R^{-}C - \stackrel{\oplus}{O} - H$$

$$H^{-} \longrightarrow R^{-}C^{+} \xrightarrow{ROH} R - \stackrel{\oplus}{O} - C^{-}R$$

$$H^{-} \longrightarrow R^{-}C^{+} \longrightarrow R^{-}O^{-} \longrightarrow H^{-}$$

$$H^{-} \longrightarrow R^{-}C^{-}OR$$

Above reaction is laboratory method of ester preparation.

Ö

2.



3 Reaction with Acid derivatives (Acetylation) :

$$\begin{array}{c} R-O-H+X-C-R \xrightarrow{Conc.H_2SO_4} R-O-C-R+HX \\ \parallel & & \parallel \\ O & O \\ Alcohol Acid halide & ester \\ R-O-H+R-C-O-C-R \xrightarrow{Conc.H_2SO_4} \\ \parallel & \parallel \\ O & O \\ Acid anhydride \end{array}$$

ester 4. Reaction with ethylene oxide :

$$R-O-H+CH_2$$
 CH2

ethylene oxide

$$\xrightarrow{\text{CH}_2 - \text{CH}_2} \xrightarrow[-H_2O]{\text{CH}_2 - \text{CH}_2} \xrightarrow[-H_2O]{\text{CH}_2 - \text{CH}_2} \xrightarrow[]{\text{CH}_2 - \text{CH}_2} \\ OR OH OR OR \\ 1, 2 - \text{dialkoxy ethane}$$

- 5. Reaction with Diazomethane :  $R \longrightarrow C \longrightarrow H + CH_2N_2 \longrightarrow R \longrightarrow CH_3$ Diazomethane (ether)
- 6. Reaction with Grignard Reagent :

$$ROH + R'MgX \longrightarrow Mg < X + R'H$$
  
Alkane

7. Reaction with Ketene :  $R - O - H + CH_2 = C^{+\delta}$ 

Ketene

1. Reaction with dry HX (Grove's Process) : Reactivity order of halogen acid is HI > HBr > HCl

$$R - OH + HX \xrightarrow{ZnCl_2} R - X (Alkyl halide) + H_2O$$

- 2. Reaction with  $PCl_5$ : R-OH+PCl<sub>5</sub>  $\longrightarrow$  R-Cl+POCl<sub>3</sub>+HCl Chloro alkane
- 3. Reaction with PCl<sub>3</sub>:  $3R \longrightarrow OH + PCl_3 \longrightarrow 3R \longrightarrow Cl + H_3PO_3$ Chloro alkane
- 4. Reaction with SOCl<sub>2</sub> (Darzen reaction) :

$$R \longrightarrow OH + SOCl_2 \xrightarrow{Pyridine} R \longrightarrow Cl + SO_2 + HCl$$
  
Thionyl chloride Chloro alkane

5. Reaction with ammonia :

$$R - OH + NH_3 \xrightarrow{anhy.ZnCl_2} RNH_2 + H_2O$$
  
Alkyl amine

6. Reaction with  $H_2SO_4$ :

(i) 
$$2C_2H_5OH + H_2SO_4 \xrightarrow{0^\circ C} (C_2H_5)_2SO_4 + 2H_2O$$
  
(Diethyl Sulphate)

(ii) 
$$C_2H_5OH + H_2SO_4 \xrightarrow{20^{\circ}C-100^{\circ}C} C_2H_5HSO_4$$
  
Ethyl hydrogen sulphate

(iii) 
$$CH_3$$
- $CH_2$ - $OH (excess) + H_2SO_4$ 

$$\xrightarrow{140^{\circ}\text{C}} \text{CH}_3\text{-}\text{CH}_2\text{-}\underset{\text{O}}{\overset{\text{O}}{\text{-}}\text{CH}_2\text{-}\text{CH}_3$$

(iv) 
$$CH_3 - CH_2 - OH + H_2SO_4 \xrightarrow{160^\circ} CH_2 = CH_2$$

(excess)

#### General reaction of Alcohols

#### 1. Oxidation :

- (i) Primary alcohol initially forms aldehyde on oxidation and on further oxidation forms respective acid.
- (ii) Secondary alcohol initially forms respective ketone on oxidation which on further oxidation forms acid of less carbon. Oxidation of ketone is slightly difficult than aldehyde due to stability so, we use strong oxidising agent for oxidation.
- (iii) Tertiary alcohols are resistant to oxidation in normal conditions but on taking strongest oxidising agent like chromic acid in dilute nitric acid then they form less carbon ketone.
- (iv) For oxidation of 1° alcohol, acidic KMnO<sub>4</sub> is used as oxidant while for 2° alcohol acidic K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is used.

$$\begin{array}{c} R - C - OH + [O] \xrightarrow{K_2 CrO_4} R - C - R + CO_2 + H_2O \\ | \\ CH_3 \\ 3^{\circ} \text{ alcohol} \end{array}$$
 (ketone of lesser carbon)

230

R



#### 2. **Reduction :**

$$R-O-H+2HI \xrightarrow{\text{Red P}} R-H+H_2O+I_2$$

3. **Dehydrogenation:** 

#### tert.alcohol 4. **Dehydration:**

The elimination of water from a compound is known as dehydration. The alcohols on dehydration yield alkene. The order of case of dehydration is :

alkene

Tertiary alcohols > Secondary alcohols > Primary alcohols. The process of dehydration is done by heating the alcohols with concentrated sulphuric acid or alumina at high temp.

$$CH_{3}CH_{2}OH \xrightarrow{Al_{2}O_{3}} CH_{2} = CH_{2} + H_{2}O$$

$$CH_{3}CH_{2}OH \xrightarrow{Conc.H_{2}SO_{4}} CH_{2} = CH_{2} + H_{2}O$$

$$Ethanol Ethene$$

Ethanol

#### **Oxidation through Fenton's Reagent :** 5.

Higher and branched alcohols are converted into diols through Fenton's reagent.

 $(FeSO_4 + H_2O_2)$  is Fenton's reagent.

$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + \overline{OH} + \dot{OH}$$

$$CH_3 - \overset{CH_3}{\underset{OH}{}^{-}C - CH_2 - H + \dot{OH}} \longrightarrow CH_3 - \overset{CH_3}{\underset{OH}{}^{-}C - \dot{CH}_2 + H_2O}$$

$$CH_3 - \overset{CH_3}{\underset{OH}{}^{-}C - \dot{CH}_2 + \dot{CH}_2 - \overset{CH_3}{\underset{OH}{}^{-}C - CH_3}$$

$$CH_3 - \overset{CH_3}{\underset{OH}{}^{-}C - \dot{CH}_2 + \dot{CH}_2 - \overset{CH_3}{\underset{OH}{}^{-}C - CH_3}$$

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

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

2, 5-Dimethyl hexandiol

Self Condensation : When alcohol is heated with sodium 6. ethoxide then by self condensation they convert into higher alcohol.

$$2CH_{3}(CH_{2})_{9}OH \xrightarrow[-H_{2}O]{O}{(CH_{2})_{7}CH_{3}} CH_{3}(CH_{2})_{9}OH \xrightarrow[-H_{2}O]{(CH_{2})_{7}CH_{3}} CH_{3}(CH_{2})_{9}OH CH_{2}OH$$

Higher alcohol

The above reaction is called as "Guerbet's Reaction".

#### GENERAL DEFINITIONS

- Fermentation : In presence of microbes like yeast break 1. down of complex organic compounds into simple compounds is called fermentation. It is an exothermic process.
- 2. Yeast is unicellular living parasite fungi.
- Enzymes : Nitrogenous high molecular weight complex 3. compound which converts complex organic compound in simple organic compound without taking part in reactions are called enzymes. They are also called as biocatalyst. They are made of protein.
- 4. They are sensitive to temperature, concentration and pH.
- Temperature at which enzymes are maximum efficient is 5. called optimum temperature. For yeast enzyme it is 20-35°C.
- They always work in dilute solution. They cannot work in 6. conc. solution.
- 7. Their working pH range is 6.5–7.5 (slightly acidic slightly basic).
- 8. Food of yeast cell is ammon. phosphate or ammonium sulphate.

#### PRIMARY, SECONDARY & TERTIARY ALCOHOL

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 gives alkene (dehydration takes place in this condition to tertiary alcohols)

**Lucas Test :** A mixture of (anhydrous  $ZnCl_2 + Conc. H_2SO_4$ ) is called as Lucas Reagent.

- 3° alcohol gives white ppt. with lucas reagent in 2–3 seconds (i) only.
- 2° alcohol takes 9-10 minutes. (ii)
- (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.

(a) 
$$R - CH_2 - OH - Red P/I_2 \rightarrow R - CH_2 - I$$

. ....

$$\xrightarrow{\text{AgNO}_2} \text{R} - \text{CH}_2 - \text{NO}_2 + \text{HNO}_2 \text{ nitrate}$$



nitrolic acid



NaOH (blue ppt.) HNO<sub>2</sub> nitrosoderivative

(c) 
$$\underset{R}{\overset{R}{\rightarrow}}C \xrightarrow{-OH} \xrightarrow{\text{Red P/I}_2} \underset{R}{\overset{R}{\rightarrow}}C \xrightarrow{-I} \xrightarrow{AgNO_2}$$

 $\xrightarrow{\text{HNO}_2}$  no. reaction.

#### Difference between methanol and Ethanol:

Methanol	Ethanol
1. When CH <sub>3</sub> OH is heated on	Ethanol does
Cu coil it gives formalin like smell.	not give formalin like smell.
2. When $CH_3OH$ is heated	No such odour
with salicylic acid in H <sub>2</sub> SO <sub>4</sub>	is given by
(conc.) then methyl salicylate	ethanol.
is formed which has odour	
like winter green oil	
3. It does not give haloform	It gives
or Iodoform test.	haloform test.

#### **IMPORTANT FACTS**

1.

2.

- Rectified spirit -[95.5% ethanol + 4.5% water] (an example of azeotropic solution)
- Absolute alcohol -[100% ethanol]
- 3. Power alcohol - [ethanol + benzene + petrol] 4.
  - [rectified spirit + 0.5 % methanol] Methylated spirit
- 5. Denatured spirit - [rectified spirit + pyridine]
- 6. Wash -[10% to 12% Alcohol]
- 7. Grain spirit -[Ethylalcohol]
- -[90%Alcohol] 8. Raw spirit
- 9. Wood spirit -[Methanol]
- 10. Boiling point of methanol is 65°C and of ethanol is 78.3°C. 11

**12.** Binary mixture — Benzene + Ethanol (boiling point  $68^{\circ}$ C) 13. Alcoholic beverages :

Drink Brandy Rum Gin Whisky Beer Champaign % of alcohol 40-50 45-55 40-45 40-50 3-6 8-10

#### **INTERCONVERSIONS**

- (1) Conversion of lower primary alcohol into higher primary alcohol.
  - (a) By cyanide synthesis :

$$\begin{array}{c} \operatorname{RCH}_2\operatorname{OH} \xrightarrow{P+I_2} \operatorname{RCH}_2I \xrightarrow{\operatorname{KCN}} \operatorname{RCH}_2\operatorname{CN} \\ \xrightarrow{4H} \operatorname{RCH}_2\operatorname{CH}_2\operatorname{NH}_2 \xrightarrow{\operatorname{HNO}_2} \operatorname{RCH}_2\operatorname{CH}_2\operatorname{OH} \end{array}$$

(b) By Grignard synthesis :

$$\operatorname{RCH}_2\operatorname{OH} \xrightarrow{P+I_2} \operatorname{RCH}_2\operatorname{I} \xrightarrow{Mg} \operatorname{RCH}_2\operatorname{MgI}$$
  
Ether

$$\xrightarrow{\text{HCHO}} \text{RCH}_2\text{CH}_2\text{OMgI} \xrightarrow{\text{H}_2\text{O}} \text{RCH}_2\text{CH}_2\text{OH}$$

(2) Conversion of higher primary alcohol into a lower primary alcohol.

$$RCH_{2}OH \xrightarrow{[0]} RCHO \xrightarrow{[0]} RCOOH \xrightarrow{NaOH}$$
$$RCOONa \xrightarrow{Soda-lime} RH \xrightarrow{Cl_{2}} RCl \xrightarrow{KOH(Aq.)} ROH$$

Conversion of 1° Alcohol to 2° alcohol : (3)

$$\begin{array}{c} CH_{3}CH_{2}CH_{2}OH \xrightarrow{SOCl_{2}} CH_{3}CH_{2}CH_{2}Cl \xrightarrow{alc.KOH} \\ n-propyl alcohol \end{array}$$

$$CH_{3}CH=CH_{2} \xrightarrow{HBr} CH_{3}CHCH_{3} \xrightarrow{aq. KOH} (CH_{3})_{2}CHOH$$

(4) Conversion of 2° Alcohol to 3° alcohol :

$$(CH_3)_2CHOH \xrightarrow{Cr_2O_7^{-2}/H^+} (CH_3)_2C=O \xrightarrow{CH_3MgBr}$$
  
isopropyl alcohol

$$(CH_3)_3 - COMgBr \xrightarrow{H_3O^+} (CH_3)_3C - OH$$
  
(intermediate) t-butyl alcohol

(5) Conversion of 1° Alcohol to 3° alcohol :

$$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2\text{OH} \xrightarrow{\text{H}_2\text{SO}_4/\Delta} & \text{CH}_3 - \text{C} = \text{CH}_2 \\ & & | \\ & \text{CH}_3 & & -\text{H}_2\text{O} & | \\ & & \text{CH}_2 \end{array}$$

iso-butyl alcohol

$$\xrightarrow{\text{HBr}} (\text{CH}_3)_3\text{CBr} \xrightarrow{\text{aq. KOH}} (\text{CH}_3)_3\text{C-OH}$$
  
t-butyl alcohol

ETHYLENE GLYCOL [Glycol] :

HOCH<sub>2</sub>—CH<sub>2</sub>OH is the simpler dihydric alcohol. **Preparation:** 

(1) From ethylene :

$$\begin{array}{c} CH_2 \\ \parallel \\ CH_2 \end{array} + [O] + H_2O \xrightarrow[KMnO_4 \text{ So ln}]{} \begin{array}{c} CH_2OH \\ \parallel \\ CH_2OH \end{array}$$

(2) From ethylene diamine :

$$\begin{array}{c} \mathrm{CH}_{2}\mathrm{NH}_{2} \\ | \\ \mathrm{CH}_{2}\mathrm{NH}_{2} \end{array} \xrightarrow{\mathrm{HNO}_{2}} \begin{array}{c} \mathrm{CH}_{2}\mathrm{OH} \\ | \\ \mathrm{CH}_{2}\mathrm{OH} \end{array}$$

(3) Industrial Methods: By Acid hydrolysis of ethylene oxide

(oxirane) 
$$(\begin{array}{c} CH_2 \\ H_2 \\ CH_2 \end{array} ) O \xrightarrow{H_2O} (\begin{array}{c} CH_2OH \\ H_2OH \\ CH_2OH \end{array}) CH_2OH$$

#### **Properties :**

- \* Colourless, syrupy liquid [b.p. 197° C] (H-bonding)
- \* Soluble in water and ethanol (H-Bonding)
- \* As toxic as methyl alcohol
- It contains two primary alcoholic groups.

\*



- Uses :
- \* Used as anti-freeze for motor car radiation [60% solution (-49°C)]
- \* Used as a solvent and preservative
- \* Used in the manufacture of oxirane
- \* Used as an explosive (glycol dinitrate)
   Chemical properties



#### GLYCEROLOR GLYCERINE OR 1,2,3-PROPANTRIOL

- It is trihydric alcohol. Obtained by replacing three hydrogen atoms from different carbon atoms of propane by three –OH groups.
- \* It contain two primary and one sec.alcoholic group.
- \* It is the most viscous liquid.
- \* It decompose on boiling at its B.P. hence purified by vacuum distillation.
- \* It is found is animal and vegetable fats and oils, which are triesters of glycerol with higher fatty acids.

#### PREPARATION

From Fat or Oil: By alkaline hydrolysis

 $\begin{array}{c} CH_{2}OCOR \\ | \\ CHOCOR + 3NaOH \longrightarrow \\ | \\ CH_{2}OCOR \\ fat or oil \end{array} \xrightarrow{\begin{array}{c} CH_{2}OH \\ CHOH \\ CH_{2}OH \end{array}} + 3RCOONa$ 

Salts of fatty acids (soap) Glycerol is obtained as a by product of soap industry

#### PROPERTIES

- Colourless, odourless, viscous (H-bonding) and hygroscopic liquid
- \* Non-toxic and sweet in taste
- \* High boiling point [290°C] [H–bonding]
- \* Soluble in water due to strong H-bonding.
- \* Glycerol molecule contains two primary (1°) and one secondary (2°) alcoholic groups.

$$\begin{array}{c|c} \alpha & \beta & \alpha' \\ CH_2 - CH - CH_2 \\ | & | & | \\ OH & OH & OH \end{array}$$

Pr. OH group are more reactive than sec. OH group

# Reactions :

(1) With  $PCl_5$ ,  $PBr_3$  and  $PI_3$ :

(a) 
$$\begin{array}{c} CH_2OH \\ | \\ CHOH + 3PCl_3 \\ | \\ CH_2OH \end{array} \longrightarrow \begin{array}{c} CH_2Cl \\ | \\ CHCl \\ CH_2Cl \end{array} + 3 POCl_3 + 3HCl \\ CH_2Cl \\ Glyceryl chloride \end{array}$$

(b) 
$$\begin{array}{c} CH_2OH & CH_2Br \\ | \\ CHOH + PBr_3 \longrightarrow CHBr & + H_3PO_3 \\ | \\ CH_2OH & CH_2Br \\ glyceryl \\ bromide \end{array}$$





#### (2) With $HNO_3$ : (TNG)



#### Note:

- (i) TNG is an yellow oily, poisonous liquid and causes head ache.
- (ii) TNG explodes violently when heated rapidly.
- (3) With acetic acid or acetyl chloride or acetic anhydride : Glycerol monoacetate, glycerol diacetate and glycerol triacetate are formed.

CH<sub>2</sub>OAc CH<sub>2</sub>OH CHOH AcOH ĊHOH or AcCl CH<sub>2</sub>ONO<sub>2</sub> CH<sub>2</sub>OH monoacetate

$$\xrightarrow{AcOH} or AcCl} CH_2OAc \qquad CH_2OAc \qquad | CH_2OAc \qquad | CHOAC \qquad | CHOAC \qquad | CHOAC \qquad | CHOAC \qquad | CH_2OAc \ | CH_2OAc \qquad | CH_2OAc \qquad | CH_2OAc \qquad | CH_2OAc \qquad$$

With Oxalic Acid: (4)

CH<sub>2</sub>OH

glycerol

(a) At 110°C formic acid is formed.

$$CH_{2}OH + HOOC - COOH$$

$$CHOH + HOOC - COOH$$

$$CHOH - H_{2}OOC - COOH + CH_{2}OOCH$$

$$CH_{2}OOC - COOH + CH_{2}OOCH$$

$$CHOH + CH_{2}OOCH + CHOH$$

CH<sub>2</sub>OH glycerol monooxalate monoformate

 $H_2O$  glycerol + formic acid

(b) At 230–260°C [Allyl alcohol is formed]

$$\begin{array}{c} \begin{array}{c} CH_2OH \xrightarrow{H}HO \\ | \\ CH_2OH \xrightarrow{H}HO \\ | \\ CH_2OH \end{array} \xrightarrow{C} C \\ | \\ CH_2OH \end{array} \xrightarrow{230^{\circ}-260^{\circ}C} \xrightarrow{CH_2 - O - CO} \xrightarrow{-2CO_2} \xrightarrow{CH_2} \begin{array}{c} CH_2 \\ | \\ | \\ CH_2OH \\ CH_2OH \end{array} \xrightarrow{CH_2OH} \xrightarrow{CH_2OH} \begin{array}{c} CH_2 \\ | \\ CH_2OH \\ CH_2OH \end{array} \xrightarrow{CH_2OH} \xrightarrow{CH_2OH} \xrightarrow{CH_2OH} \begin{array}{c} CH_2 \\ | \\ CH_2OH \\ CH_2OH \end{array} \xrightarrow{CH_2OH} \xrightarrow$$

glycerol dioxalate (5) With KHSO<sub>4</sub> or P<sub>2</sub>O<sub>5</sub> (Dehydration)

$$\begin{array}{ccc} CH_2OH & CH_2 \\ | \\ CHOH & \underline{KHSO_4} & CH \\ | \\ CH_2OH & -2H_2O & | \\ CHO \end{array}$$

acraldehyde  $(\alpha, \beta$ -unsaturated aldehyde)

#### USES:

- \* Used in the preparation of non-drying, printing and stamp pad inks.
- \* Used as anti freeze in automobile radiators.
- \* Used in the manufacture of various compounds e.g. formic acid, acrolein etc.
- \* Used in the manufacture of explosives such as dynamite, cordite by the help of TNG.
- \* Used in making bath soaps, hand lotions, vanishing creams etc.
- \* Used in the manufacture of plastic and synthetic fibres.
- \* Used as a sweetening agent in beverages & confectionery.

#### **TESTS:**

- Glycerol + KHSO<sub>4</sub>  $\xrightarrow{\Delta}$  offensive odours of acrolein \*
- \* 5 ml aqueous Borax solution + (one drop) phenolphthalein makes pink colour solution on adding glycerol pink colour disappears (Dunstan Test).

#### **TRY IT YOURSELF-1**

Which of the following has the lowest solubility in water? Q.1

$$\begin{array}{c} \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & & \begin{array}{c} & & \\ & & \end{array} \\ & & \end{array} \\ (A) \ CH_3CH_2CH_2CH_2OH & (B) \ CH_3 - CHC \ H_2OH \\ (C) \ HOH_2C - CH_2OH & (D) \ C_6H_5CH_2CH_2OH \\ Ethanol is heated with concentrated \ H_2SO_4. \ The product formed is - \\ & \begin{array}{c} (A) \ CH_3 - C - O - C_2H_5 & (B) \ C_2H_6 \\ & O \end{array} \\ \end{array}$$

(

allyl alcohol



benzene)

Phenol



OH  $CH_2OH$   $O-CH_3$ 

o-, m- and p-Cresols Benzyl alcohol Anisole Similarly, dihydroxybenzene (dihydric phenols) may exist in three isomeric forms.



ΕΤΊΔΟΝς ΟΕ ΡΟΕΡΑ Ο ΑΤΙ

METHODS OF PREPARATION(i) By fusing the sodium salt of benzenesulphonic acid with

benzene)



Benzenesulphonic Sod. benzene acid sulphonate

ii) By adding benzene diazonium chloride to a large volume of boiling dilute  $H_2SO_4$ .



Benzenediazoniumchloride Phenol

(iii) By heating chlorobenzene with caustic soda under pressure (**Dow's process**). This is commercial method. The reaction involves nucleophilic substitution.





#### (7) (B) (8) (A) (10) (B)

#### INTRODUCTION

(4) (A)

Compounds in which hydroxyl group is directly attached to the benzene nucleus are known as phenols.

(5) (A)

**PHENOLS** 

(6) (D)

(9) (D)





(iv) From cumene hydroperoxide

$$C_6H_6 + CH_3CH = CH_2 \xrightarrow{AlCl_3} C_6H_5 - CH_1$$

Benzene Propene Cumene

$$\xrightarrow[CH_3]{0} C_6H_5 \xrightarrow[-C-O-O-H]{H_3O^+} C_6H_5OH + (CH_3)_2CO$$

Cumene hydroperoxide Phenol Acetone By distilling a phenolic acid with soda lime. (v)



Salicylic acid

#### (vi) By Raschig process :

$$C_{6}H_{6} + HCl + \frac{1}{2}O_{2} \xrightarrow{Cu-Fe} C_{6}H_{5}Cl + H_{2}O$$

$$C_{6}H_{5}Cl + HOH \xrightarrow{SiO_{2}} C_{6}H_{5}OH + HCl$$

#### PHYSICAL PROPERTIES

(i) Colourless crystalline solid with carbolic smell.

(ii)  $m.p. = 40^{\circ}C \quad b.p. = 182^{\circ}C$ 

- (iii) Turns pinkish when exposed in air.
- (iv) Soluble in organic solvent, partially soluble in cold water.

#### **CHEMICAL PROPERTIES**

#### Acidic character (Salt formation) :

Unlike alcohols, phenols are acidic in nature and react with alkali metals and their hydroxides to form salts known as phenoxides or phenates. However, phenols do not react with weak alkalies like carbonates or bicarbonates (difference from carboxylic acids).

$$\begin{array}{ccc} 2C_{6}H_{5}OH+2Na \longrightarrow 2C_{6}H_{5}ONa+H_{2} \\ Phenol & Sod. \ phenate \\ C_{6}H_{5}OH+NaOH \longrightarrow C_{6}H_{5}ONa+H_{2}O \end{array}$$

In short, phenols are stronger acids than alcohols but weaker than the carboxylic acids.

#### **Reaction of – OH group :**

- Action of ferric chloride : Unlike alcohols, phenols give (i) characteristic colour with neutral ferric chloride solution. The characteristic colour is believed to be due to the formation of coloured co-ordination compounds. Reaction of phenols with ferric chloride is used in analytic chemistry for distinguishing phenols from carboxylic acids.
- (ii) Reduction with zinc dust : Phenols, when distilled with zinc dust, give aromatic hydrocarbon.

$$C_6H_5OH + Zn \xrightarrow{distil} C_6H_6 + ZnO$$
  
Phenol Benzene

- (iii) Alkylation: (a) Phenol is alkylated to give Phenolic ethers is the presence of alkali with alkyl halides for example

Benzene

$$\bigcirc H + \text{NaOH} + \text{CH}_3\text{I} \rightarrow \bigcirc H + \text{H}_2\text{O} + \text{NaI}$$

Methylphenylether or Anisole or Methoxybenzene

$$\overset{OH}{\longleftarrow} + C_2 H_5 I \xrightarrow{\text{NaOH}} \overset{OC_2 H_5}{\longleftarrow} + \text{NaI} + H_2 O$$

Ethylphenylether or Phenetole or Ethoxy benzene

(b) Phenol can be methylated by treatment with diazomethane.

$$(Anisole) + N_2^{+}$$

(iv) Acylation:

$$\overset{OH}{\longmapsto} + CH_3COCl \xrightarrow{\text{NaOH}} + NaCl + H_2O$$

Phenol Acetyl chloride

Phenyl acetate

Reaction with PCl<sub>5</sub>: Chlorobenzene is formed in low yield (v) and mainly triphenyl phosphate is formed.



Chorobenzene Phenol  $3C_6H_5OH + POCl_3 \longrightarrow (C_6H_5)_3PO_4 + 3HCl$ (Triphenylphosphate)

(vi) Reaction with NH<sub>3</sub>: Aniline is obtained

$$\underbrace{OH}_{\text{Phenol}} + \text{NH}_3 \xrightarrow{\text{ZnCl}_2 \text{ anhyd}}_{300^{\circ}\text{C}} \underbrace{OH}_{\text{Aniline}} + \text{H}_2\text{O}$$

Aniline

#### **Reaction of Benzene ring :**

The -OH group in phenol, being activating group, facilitates further substitution in the ortho and para positions. In fact, the –OH group is so highly activating that unless precautions are taken, polysubstitution takes place.



Halogenation : Phenols when treated with aqueous solution (i) of halogens undergo halogenation very rapidly to form polyhalogene derivatives. For example,



2, 4, 6-Tribromophenol (white ppt.)

In fact, phenols are so reactive towards bromine water that even substituent like - SO<sub>2</sub>H, - NO<sub>2</sub>, - COOH, etc. if present, in o-and p-positions, may be replaced by halogens. Polyhalogenation while using water as solvent is because of the fact that water (a highly polar solvent) facilitates the ionisation of phenol to phenoxide ion which is more reactive than phenol towards electrophilic substitution.

For preparing monohalogeno derivatives, halogenation is carried out at low temperature and in non-polar solvents such as carbon tetrachloride or carbon disulphide. For example,



Phenol

o-Bromophenol) p-Bromophenol (major)

Non-polar solvents (CS2, CCl4) decreases the electrophilic character of Br<sub>2</sub> and minimizes ionization of phenol.

(ii) Nitration : With dilute nitric acid, phenol giving a mixture of o- and p- nitrophenols. The relatively low yields are due to oxidation of phenol by nitric acid. Since o-nitrophenol is more volatile than the para, the two isomers can be separated by steam distillation.

(minor



Nitrophenol (40%) p-Nitrophenol (~10%) Nitration of phenol with concentrated nitric acid or a nitrating reagent gives 2, 4, 6-trinitrophenol (picric acid). However, the yield is low because of excessive oxidation of phenol.



(iii) Sulphonation : Sulphonation of phenols occurs readily giving a mixture of o- and p- isomers; o-isomer predominates at low temperature while p-isomer at high temperatures. Further, the o-isomer can be changed to p-isomer on heating.



p-Phenolsulphonic Phenol

o-Phenolsulphonic acid

Friedel - Craft reaction : Phenols undergo Friedel-Craft (iv) alkylation and acylation forming predominantly para isomers. However, the yields are poor presumably due to overactivity of phenols.

(a) Alkylation



(b) Acylation



#### (v) Kolbe reaction :

When sodium salt of a phenol is heated with carbon dioxide gas at 120–140°C under pressure (6–7 atmospheres), a carboxyl group is introduced mainly in the ortho position with respect to the phenolic group to form o-hydroxy benzoates. This reaction is known as Kolbe reaction. A small amount of p-isomer is also obtained. However, if the reaction is carried out at high temperature, p-isomer is the main product.



(vi) Riemer-Tiemann reaction : (reaction between phenol and alkaline chloroform or carbon tetrachloride to form salicylaldehyde and salicylic acid respectively).

237





(vii) Gattermann's reaction : Phenol when treated with liquid hydrogen cyanide and HCl gas is presence of anhydrous AlCl<sub>3</sub> yields mainly p-hydroxy benzaldehyde [formylation].

$$HCI+H-C \equiv N \xrightarrow{HCI_3} CI-HC = NH$$

$$OH \xrightarrow{OH} + CIHC = NH \xrightarrow{AICI_3} OH \xrightarrow{OH} (-HCI) \xrightarrow{H_2O} OH \xrightarrow{OH} (-NH_3) \xrightarrow{OH} CHO$$

(p-hydroxy benzaldehyde)

#### (viii) Mercuration :

AlCla

Phenol when heated with mercuric acetate undergoes mercuration to form o- & p-isomers.





#### (ix) Hydrogenation:

Phenols when hydrogenated in presence of nickel catalyst at about 150–200°C give the corresponding cyclohexanol.



## Phenol

#### **Miscellaneous Reactions :**

#### **Coupling reaction :** (i)

Phenol reacts with benzene diazonium chloride in presence of an alkaline solution to form a red dye (p-Hydroxyazobenzene).



#### (ii) Phthalein Reaction :

Phenol reacts with phthalic anhydride in presence of concentrated  $H_2SO_4$  to form phenolphthalein.



#### Phenol (2 molecules) (iii) Condensation with formaldehyde:

Phenolphthalein (a dye)

Phenol react with HCHO in weak acidic or alkaline medium to form a mixture of o- and p-Hydroxy benzyl alcohol. The reaction is called Lederer-Manasse reaction. These products further condense to give a crossed linked polymer known as bakelite.







Bakelite (a resin)



#### **Oxidation:**

(iv) With Acetone :

Phenol turns pink or red or brown on exposure to air and (i) light due to slow oxidation. The colour is probably due to the formation of p-benzoquinone.



238







#### TESTS

(i) Phenol + FeCl<sub>3</sub> [neutral]  $\longrightarrow$  Violet colour (ii) Bromine water + phenol  $\longrightarrow$  white precipitate

(iii) Blue litmus + phenol  $\longrightarrow$  red

#### Libermann's nitroso test :

Phenol  $\xrightarrow{\text{NaNO}_2}$  Green colouration  $\xrightarrow{\text{H}_2\text{O}}$ 

Red colouration  $\xrightarrow{\text{NaOH}}$  Blue colouration

#### USES:

(i) In the formation of bakelite plastic

- (ii) Manufacturing of dyes.
- (iii) In the formation of phenolphthalein.
- (iv) As antiseptic and germicidal.
- (v) In the preparation of aspirin, salol, methyl salicylate.
- (vi) In the manufacturing of picric acid.

#### **TRY IT YOURSELF-2**

**Q.1** Dow's process used in the industrial preparation of phenol, is

(A) 
$$C_6H_5Cl \xrightarrow{NaOH} C_6H_5OH + NaCl$$

(B) 
$$C_6H_5Cl + H_2O \xrightarrow{SO_2}{425^{\circ}C} C_6H_5OH + HCl$$

(C) 
$$C_6H_5NH_2 + HNO_2 \xrightarrow{\Delta} C_6H_5OH + N_2 + H_2O$$

(D)  $C_6H_5N_2Cl + H_2O \rightarrow C_6H_5OH + N_2 + HCl$ 

- Q.2 Which of the following is not a phenolic compound (A) Salol (B) o-Cresol (C) Anisole (D) Quinol
- Q.3 Unacceptable name for a compound containing one OH group attached to benzene nucleus would be –
  (A) Carbolic acid (B) Hydroxybenzene
  (C) Catechol (D) Phenol
- Q.4 How many  $\pi$  electrons are there in a planar ring of phenol (A) 4 (B) 6 (C) 8 (D) 10
- Q.5 In phenols
  - (A) OH group is attached in side chain.
  - (B) OH group is directly attached to benzene nucleus.(C) Both (A) & (B)
  - (D) None
- **Q.6** Which of the following will not be soluble in sodium carbonate solution –





	(A) Anisol from phenol		
	(B) Salicylaldehyde from phenol and CHI <sub>3</sub>		
	(C) Salicylic acid from soc	lium phenate and $CO_2$ .	
	(D) Salicylic acid from phe	enol and $CO_2$ .	
Q.8	p-Nitrophenol is stronger a	cid than phenol because nitro	
	group is –		
	(A) Electron withdrawing	(B) Electron donating	
	(C) Basic	(D) Acidic	
Q.9	The product obtained by	the reaction of phenol with	
	benzene diazonium chloride is –		
	(A) Phenyl hydroxyl amine	e (B) Para amino azobenzene	
	(C) Phenyl hydrazine	(D) Parahydroxy azobenzene	
Q.10	Phenol is converted into sa	alicylaldehyde by –	
	(A) Etard reaction	(B) Kolbe reaction	
	(C) Reimer-Tiemann reaction (D) Cannizzaro reaction		
	ANSW	ERS	
	(1) (A) (2)(C)	<b>(3)</b> (B)	

Kolbe's reaction consists in obtaining -

(-) (-)	(-)(-)	$(\mathbf{U})(\mathbf{U})$
(4) (C)	<b>(5)</b> (B)	<b>(6)</b> (C)
(7) (C)	<b>(8)</b> (A)	<b>(9)</b> (D)
(10)(C)		

#### ETHERS

#### GENERALCHARACTER

- (a) Ether (R—O—R) is a dialkyl derivative of water or alkoxy derivative of alkane or anhydride of alcohols.
- (b) General formula is  $C_n H_{2n+2}O$

Q.7

(c) Bond angle is 110° due to counter balance repulsion of alkyl groups. Hybridisation state of oxygen is sp<sup>3</sup>

sp<sup>3</sup> Hybridisation

- (d) Carbon oxygen bond length is 1.42 Å.
- (e) If both alkyl groups are similar then these are called as simple ether (R O R) if different they are called as mixed ether [R O R'].
- (f) In IUPAC system ethers are called as "Alkoxy alkane".

#### **METHODS OF PREPARATION**

#### Williamson's continous Etherfication process :

Excess of ethanol reacts with conc.  $H_2SO_4$  at 140° C and forms ethoxy ethane.

$$CH_3$$
— $CH_2$ — $OH$  (Ethanol) + conc.  $H_2SO_4$ 

$$\xrightarrow{100^{\circ}} CH_3 - CH_2 - HSO_4 + H_2O$$

Ethyl hydrogen sulphate

$$CH_{3} - CH_{2} - HSO_{4} + H_{1} - O - CH_{2} - CH_{3}$$

$$\xrightarrow{140^{\circ}} CH_{3} - CH_{2} - O - CH_{2} - CH_{3} + dil. H_{2}SO_{4}$$
ether

**Williamson Synthesis :** When ethyl halide reacts with sodium ethoxide then ether is formed. Mechanism of the reaction is based on Nucleophilic Substitution.

$$\mathbf{R} - \begin{bmatrix} \mathbf{X} + \mathbf{N}\mathbf{a} \end{bmatrix} \mathbf{O}\mathbf{R} \longrightarrow \mathbf{R} - \mathbf{O} - \mathbf{R} + \mathbf{N}\mathbf{a}\mathbf{X}$$

240

\_ \_ \_ \_ \_ \_



$$CH_3 - CH_2 - H_1 + Na + O - CH_2 - CH_3$$
  
Ethyl Iodide Sodium Ethoxide  
$$\rightarrow CH_3 - CH_2 - O - CH_2 - CH_3 + NaI$$

Other Example %

- \* Sodium tert-butoxide + ethyl bromide
   Product → tert. butyl ethyl ether
- \* Sodium phenoxide + methyl bromide Product  $\rightarrow$  anisole

\* 
$$\bigcirc$$
 Br + CH<sub>3</sub>ONa  $\rightarrow$  No reaction

#### By Reaction of Ethyl Iodide with dry Ag<sub>2</sub>O:

 $CH_2 - CH_2 - I + Ag + O - Ag - I + CH_2 - CH_3$   $\longrightarrow CH_3 - CH_2 - O - CH_2 - CH_3 + 2AgI$   $CH_3 - I + Ag - O - Ag + I - CH_2 - CH_3$   $\longrightarrow CH_3 - O - CH_2 - CH_3 + 2AgI$ 

#### **Industrial Methods :**

(a) 
$$2C_2H_5OH \xrightarrow{Con.H_2SO_4} C_2H_5-O-C_2H_5+H_2O$$
  
 $140^{\circ}$ 

(b) 
$$2C_2H_5OH \xrightarrow{Al_2O_3}{250^\circ C} C_2H_5-O-C_2H_5+H_2O$$

#### PHYSICAL PROPERTIES

- (i) Ethers are colourless with specific smell liquid.
- (ii) These are highly volatile liquid due to low boiling point.
- (iii) These are insoluble in water although they have oxygen atom, but their oxygen atom is neutral due to steric hindrance of both alkyl groups.
- (iv) Boiling point of diethyl ether is 307.6 K.

#### **CHEMICAL PROPERTIES**

#### Halogenation :

(i) In dark : Halogen reacts with ether in dark and substitutes  $\alpha$  and  $\alpha$ ' hydrogen atoms.

$$C\overset{\beta'}{H_3} - C\overset{\alpha'}{H_2} - O - C\overset{\alpha}{H_2} - C\overset{\beta}{H_3} + 2Cl - Cl$$

$$\xrightarrow{dark} CH_3 - CH - O - CH - CH_3 + 2HCl$$

$$\overset{l}{Cl}$$

 $\alpha, \alpha$ '-dichlorodiethyl ether

#### (ii) In Light

 $CH_3-CH_2-O-CH_2-CH_3+10Cl_2$   $\xrightarrow{hv} CCl_3-CCl_2-O-CCl_2-CCl_3+10HCl$ perchloroether

#### **Oxidation :**

When ether is left open in air, it reacts with atmospheric oxygen and forms peroxide.

$$\begin{array}{c} CH_{3}-CH_{2} \\ CH_{3}-CH_{2} \end{array} \rightarrow \begin{array}{c} + \frac{1}{2}O_{2} \longrightarrow \begin{array}{c} CH_{3}-CH_{2} \\ CH_{3}-CH_{2} \end{array} O \xrightarrow{C}_{2}C_{2}H_{5}-O-O-C_{2}H_{5} \\ ether peroxide \end{array}$$

When ether is exposed to air for a long time then the above peroxide changes into another peroxide which is called as "Ethoxy ethyl hydroperoxide' and is more explosive in nature.

$$C_{2}H_{5}-O-O-C_{2}H_{5} + \frac{1}{2}O_{2} \rightarrow C_{2}H_{5} - O-C-CH_{3}$$

$$O-O-H$$
ethoxy ethyl hydroperoxide

#### Test for peroxide in the ether

[Ether + freshly prepared FeSO<sub>4</sub> solution + Few drops of KCN]—Red colour [Fe(CNS)<sub>3</sub>]

Appearance of red colour confirms the presence of peroxide **Combustion :**-

 $Fe^{+2} \xrightarrow{\text{peroxide}} Fe^{+3} \xrightarrow{\text{KCNS}} \text{Red colour } [Fe(CNS)_3]$ 

**Note :** When ether is oxidised with acidic  $K_2Cr_2O_7$  then it forms aldehyde.

#### **Reaction with HX :**

#### (a) If HX is cold :

 $CH_3 - O - CH_2 - CH_3 + HX(cold) \rightarrow CH_3 - X + C_2H_5OH$ **Note :-** If we take unsymmetrical ether with cold H—X then smaller alkyl group forms alkyl halide.

#### (b) If HX is hot :

 $\xrightarrow{\Lambda}$  2CH<sub>3</sub>-CH<sub>2</sub>-X+H<sub>2</sub>O

 $CH_3$ -O- $CH_2$ - $CH_3$ +2H-X  $\xrightarrow{\Delta}$   $CH_3$ -X+ $C_2H_5$ X+H<sub>2</sub>O **Note :** The above reaction is called 'Ziesel's Method of Alkoxy group estimation'. If we take unsymmetrical ether with hot H – X then we get two different types of alkyl halide and by the test of both alkyl halide we can confirm alkoxy group of ether.

**Reaction with PCl<sub>5</sub>:**  $C_2H_5 - O - C_2H_5 + PCl_5 \longrightarrow 2C_2H_5Cl + POCl_3$ 

**Reaction with Acetyl Chloride :** 

$$C_{2}H_{5} \rightarrow O \xrightarrow{+C_{2}H_{5}+|Cl|} \xrightarrow{-C} -CH_{3}$$

$$0$$

$$\xrightarrow{dry \ ZnCl_{2}} \rightarrow CH_{3} - C - O - C_{2}H_{5} + C_{2}H_{5}Cl$$

$$0$$

$$0$$



#### **Reaction with Carbon monoxide (carbonylation) :**

$$C_{2}H_{5} - O - C_{2}H_{5} + \underset{\times}{\overset{\times}{\times}}CO$$

$$\xrightarrow{BF_{3}} C_{2}H_{5} - C - O - C_{2}H_{5}$$

**Note** : In the case of unsymmetrical ether, CO–group attaches with the bigger alkyl group. **Reduction :** 

$$C_2H_5-O-C_2H_5+2H \xrightarrow{\text{Na/liq.NH}_3} C_2H_6+C_2H_5-OH$$

Reaction with H<sub>2</sub>SO<sub>4</sub>: With conc. H<sub>2</sub>SO<sub>4</sub>

 $\begin{array}{c} C_2H_5 & \longrightarrow \\ C_2H_5 + 2H_2SO_4 & \xrightarrow{\Delta} 2C_2H_5HSO_4 + H_2O \\ & \hline \\ Ethyl hydrogen sulphate \end{array}$ 

With dil. H<sub>2</sub>SO<sub>4</sub> : **(b)** 

$$C_2H_5 - O - C_2H_5 + H - OH \xrightarrow{dil.H_2SO_4} C_2H_5OH$$

#### **Dehydration:**

When vapours of ether are passed on 380° C heated alumina then by the elimination of water alkene is formed :



#### **Preparation of Oxonium Salt :**

Oxygen of ether has lone pair of electron so it can form salt with mineral acid or lewis acid by forming coordinate bond with it. Such type of salt is called Oxonium Salt.







boron trifluoride etherate

#### Combustion %

$$C_2H_5O - C_2H_5 + 6O_2 \rightarrow 4CO_2 + 5H_2O$$

#### Electrophilic substitution reactions of Anisole :

- OCH<sub>3</sub> group is a ortho and para directing group. Some reactions are





#### USES

0.2

- 1. Wurtz reaction
- Alcohol + ether  $\rightarrow$  Natelite  $\frac{1}{4}$ Used in place of petrol $\frac{1}{2}$ 2.
- 3. Ether is also called as inert solvent of aliphatic chemistry, due to inertness of oxygen.
- 4. Due to inertness of oxygen, it is best solvent for preparation of highly reactive compounds such as G.R.
- 5. It is used as an anesthetic. Other compounds such as ethrane and isoflurane also used as an anaesthetic.

$$\begin{array}{c} F \\ CI \\ F \\ CH - C - O - CHF_2 \\ F \\ F \\ F \\ F \\ CI \\ \end{array} \qquad \begin{array}{c} CF_3 - CH - O - CHF_2 \\ CI \\ CI \\ \end{array}$$

Ethrane

isoflurane

#### **TRY IT YOURSELF-3**

- The number of alkanols and ethers represented by the 0.1 molecular formulae C3H8O and C4H10O respectively are given by the set -
  - (A) 2, 1; 3, 2 (B) 1, 2; 2, 3
  - (C) 2, 1; 4, 3 (D) 2, 1; 3, 4 Anhydrides of alcohol are nothing but
  - (A) Ethers (B) Aldehydes
  - (C) Esters (D) Alkyl anhydrides
- In which case the product is neither a cyclic ether nor Q.3 open chain symmetrical ether -

(A) 
$$CH_3 - CH = CH - CH_3 \xrightarrow{C_6H_5CO_3H}$$

(B) 
$$CH_3CH_2ONa + C_2H_5Br -$$

(C) KCN+(CH<sub>3</sub>)<sub>3</sub>CBr  $\rightarrow$ 

(D) 
$$C_2H_5OH$$
 (excess) +  $H_2SO_4$   $\xrightarrow{140^{\circ}C}$ 

- For making  $(CH_3)_3C O C_2H_5$  the ideal combination is 0.4 (A)  $(CH_3)_3CONa \& C_2H_5Br (B) (CH_3)_3CBr \& C_2H_5ONa$ (C) Both of these (D) None of these
- Q.5 Diethyl ether acts as a -(A) Lewis acid
  - (B) Lewis base
  - (C) Reducing agent (D) Oxidising agent
- The compound obtained by the reaction of diethyl ether Q.6 chlorine in the presence of sunlight, is -
  - (A) Perchloro diethyl ether  $H_5C_2 OC_2Cl_5$
  - (B) Perchloro diethyl ether  $Cl_5C_2 OC_2Cl_5$
  - (C)  $\beta$ ,  $\beta$  '-Dichloro diethyl ether ClCH<sub>2</sub>CH<sub>2</sub>-O-CH<sub>2</sub>CH<sub>2</sub>Cl
  - (D)  $\alpha, \alpha'$ -Dirchlorodiethylether

$$\begin{array}{c} CH_3 - CH - O - CH - CH_3 \\ | \\ Cl \\ Cl \\ Cl \end{array}$$

- Q.7 Diethyl ether absorbs oxygen to form -
  - (A) Red coloured sweet smelling compound.
  - (B) Acetic acid
  - (C) Ether suboxide
  - (D) Ether peroxide

- Q.8 Ether does not form oxonium salt on reaction with -(A) Conc conc.  $H_2SO_4$ (B) Cold conc. HCl (C) Conc. HI (D) None of the above
- 0.9 Unsymmetrical ethers are best prepared by -(A) Willamson's continuous etherification process. (B) Reacting Grignard reagent with alkyl halide.
  - (C) Treating sodium alkoxides with alkyl bromides.
  - (D) Heating an alkanol with conc.  $H_2SO_4$ .
- Q.10 The structure of the compound formed by the reaction of diethyl ether with oxygen of air is -(A)  $CH_3CH_2 - O - O - CH_2CH_3$

- (B)  $CH_3CH_2 O CH O O H$
- (C)  $CH_3CH_2 O O CH_2 O CH_3$
- (D)  $CH_2(OCH_3) CH_2 O-C_2H_5$

	<u>ANSWERS</u>	
(1) (C)	<b>(2)</b> (A)	<b>(3)</b> (C)
(4) (A)	<b>(5)</b> (B)	<b>(6)</b> (B)
(7) (D)	<b>(8)</b> (C)	<b>(9)</b> (C)
<b>(10)</b> (B)		

## ADDITIONAL EXAMPLES

Example 1 :

Which of the following has the highest value of pK<sub>a</sub>?  $(A) CH_3 - CH_2OH$  $(B) Cl - CH_2 - CH_2OH$ 

(C) 
$$F_3C - CH_2 - OH$$
 (D)  $CH_3 - CH - CH_2OH$ 

**(D).** Acidic nature  $\propto \frac{1}{pk_a - value}$ Sol.

> Acidity of  $CH_3 - CH - CH_2OH$  is minimum due to CH<sub>3</sub>

+I-effect isopropyl group.

Example 2 :

(A) 
$$CH_3 - CH_2 - CH - CH_3(B) CH_3 - CH_2 - CH_2 - CH_2OH$$

au

(C) 
$$CH_3 - CH - CH_2OH$$
 (D)  $CH_3 - C - OH$   
 $| CH_3 - CH_3 - C - OH$   
 $| CH_3 - CH_3 - CH_3$ 

(B). Due to effective hydrogen bonding boiling point of Sol. unbranched alcohol is more than branched chain alcohol.



 $3^{\circ} > 2^{\circ} > 1^{\circ}$ 

#### Example 3 :

The compound which reacts faster with Lucas reagent at room temperature is – (A) butan-1-ol (B) butan-2-ol (C) 2-methyl propan-1-ol (D) 2-methyl propan-2-ol **Sol.** (D). Reactivity order of alcohol with Lucas reagent

#### Example 4 :

The hydroboration oxidation of 2-methyl propene yields(A) 1° alcohol(B) 2° alcohol(C) 3° alcohol(D) None

Sol. (A). 
$$CH_3 - CH = CH_2 \xrightarrow{(i) BH_3 - THF/HOH} (ii) H_2O_2/NaOH$$

 $CH_3 - CH - CH_2$ 1° alcohol

This is a method of addition of HOH molecule by Anti-Markovnikov's rule.

#### Example 5 :

Which of the following isomeric alcohols have highest melting and boiling points – (A) Primary (B) Secondary

<i>T</i> () I IIIIai y	(D) Secondary
C) Tertiary	(D) All equal

**Sol.** (A). Melting point and boiling point of branched chain alcohols are less than unbranched chain alcohol.

#### Example 6 :

Alkyl chloride is formed when alcohol is treated with HCl in presence of anhydrous  $\text{ZnCl}_2$ . The order of reactivity with respect to alcohol is –

(A)  $3^{\circ} > 2^{\circ} > 1^{\circ}$  (B)  $1^{\circ} > 2^{\circ} > 3^{\circ}$ (C)  $2^{\circ} > 1^{\circ} > 3^{\circ}$  (D)  $1^{\circ} > 3^{\circ} > 2^{\circ}$ 

Sol. (A). Reactivity order of alcohols with HCl + ZnCl<sub>2</sub> (Lucas reagent) is  $3^{\circ} > 2^{\circ} > 1^{\circ}$ , because stability of

carbocation of alcohol is  $3^{\circ} > 2^{\circ} > 1^{\circ}$ .

#### Example 7 :

A compound X with molecular formula  $C_3H_8O$  can be oxidised to a compound Y with the molecular formula  $C_3H_6O_2$ , X is most likely to be –

(A) Primary alcohol	(B) Secondary alcohol
(C) Aldehyde	(D) Ketone
( ) )	





#### Example 8 :

Phenol and benzoic acid can be distinguished by – (B) Aqueous NaNO<sub>3</sub> (C) Aqueous NaOH (D) Conc.  $H_2SO_4$ 

Sol. (A). Due to more acidic nature of benzoic acid, benzoic acid show efferevecense due to release of  $CO_2(\uparrow)$  from NaHCO<sub>3</sub>.

#### Example 9:

Which of the following is a cyclic ether –

(A) Ethyl ether
(C) Phenyl ether

- ether (B) Vinty ether
  - (D) Tetrahydrofurane



Tetrahydrofuran (A cyclic ether of 5 member)

#### Example 10:

- In order to obtain diethyl ether from ethanol, the latter is taken in –
- (A) In equal amount of sulphuric acid
- (B) In slightly lesser amount of sulphuric acid
- (C) In excess amount of sulphuric acid
- (D) In far lesser amount of sulphuric acid

Sol. (C). 
$$CH_3 - CH_2 - OH \xrightarrow{H_2SO_4/\Delta}$$
 Excess amount

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

#### Example 11 :

In the Williamson's synthesis for diethyl ether, which species works as a nucleophile –

- (A) Halide ion(B) Ethoxide ion(C) Ethyde ion(D) Hydride ion
- Sol. (B).  $CH_3 CH_2 Br + NaOC_2H_5$ Sodium ethoxide (As-Nucleophile)

 $\longrightarrow C_2H_5 - O - C_2H_5$ Diethylether



#### Example 12:

What are the final products of the following sequence of reactions?

$$C_6H_6 + CH_3CH = CH_2$$

$$\xrightarrow{\text{Anhy. AlCl}_3} ? \xrightarrow{\text{O}_2/130^\circ\text{C}} ? \xrightarrow{\text{H}^+} ?$$

- (A) Cumene and phenol
- (B) Phenol and acetone
- (C) Cumene and acetone
- (D) Benzoic acid and ethane



#### Example 13 :

The product of the reaction of benzene with oxygen in the presence of  $V_2O_5$  as catalyst at 200°C is – (A) Maleic anhydride (B) Benzoic acid

OH

(C) Phenol (D) None of these



(C) Aniline

#### Example 14 :

Phenol on treatment with ammonia gives – (A) Benzene (B) Benzoic acid

(D) None



#### Example 15 :

 $\label{eq:conditions} \begin{array}{l} C_6H_5CH_2OH~(A)~C_6H_5OH~(B),\\ \text{and}~C_6H_5COOH~(C)~\text{can act as acids.}~\text{The increasing order}\\ \text{of their acidic strength is}-\\ (A)~A < B < C \\ \end{array} \\ \begin{array}{l} (B)~A < C < B \\ \end{array}$ 

- $(C) B < A < C \qquad (D) C < B < A$
- Sol. (A). Acidic nature of Ph–COOH is more than Ph OH than because the stability of conjugate base of Ph COOH is more stable than Ph OH and that ph OH is more than benzyl alcohol Ph CH<sub>2</sub> OH.

#### Example 16 :

The most s	suitable metl	hod of	separation	n of a 1	: 1 mixtu	ıre
of o- and j	o-nitropheno	ol is –				
(1) 0 11						

- (A) Sublimation (B) Chromatography (C) Crystalliastion (D) Distillation
- Sol. (D). Due to intramolecular hydrogen bond (chelation) boiling point of o-nitrophenol is less than p-nitrophenol. So they can be separated by distillation.

#### Example 17:

Diethyl ether is metamer of -(A) Ethoxyethane(B) N(C) Methoxyethane(D) E

- (B) Methyl propyl ether (D) Ethoxymethane
- Sol. (B).  $CH_3 CH_2 O CH_2 CH_3$ Diethylether

& 
$$CH_3 - O - CH_2 - CH_2 - CH_3$$
  
Methylpropylether

Metamers

(because alkyl group attached with 'O' in both ether are different).

#### Example 18:

The correct combination of names for isomeric alcohols with molecular formula  $C_4 H_{10}O$  is/are

- (A) Tert-butanol and 2-methylpropan-2-ol.
- (B) Tert-butanol and 1, 1-dimethylethan-1-ol.
- (C) n-butanol and butan-1-ol.

(D) Isobutyl alcohol and 2-methylpropan-1-ol.

Sol.(ACD).Common nameIUPAC name(A) $\checkmark^{OH}$ tert-butanol2-methylpropanol(C) $\sim_{OH}$ n-butanolbutan-1-ol(D) $\sim_{OH}$ isobutyl alcohol2-methyl propan-1-ol

#### Example 19 :

The increasing order of boiling points of the alcohols is

(I) 1, 2-dihydroxybenzene	(II) 1, 3-dihydroxybenzene
(III) 1, 4-dihydroxybenzene	(IV) Hydroxybenzene
(A) I < II < IV < III	(B) I < II < III < IV
(C) IV < II < I < III	(D) $IV < I < II < III$

Sol. (D). Among the given compounds, hydroxybenzene (IV) has least molar mass and therefore possess least boiling point. Among the three isomeric dihydroxybenzenes. 1-2-dihydroxybenzene (I) forms intramolecular H-bonding with the result it will not form intermolecular H-bonding leading to lowest boiling point. On the other hand the 1-4-dihydroxybenzene (III) does not undergo chelation, hence it will involve extensive intermolecular H-bonding leading to highest boiling point. Thus the decreasing order of boiling points is III > II > I > IV.



Q	<b>UESTION BANK</b>		10 : AL	COHOLS, PHENOLS AND ETHERS
	EXERCISE - 1 [LEVEL-1]			
Choo	se one correct response for ea	ich question.	PA	RT - 2 : STRUCTURES OF FUNCTIONAL
	PART - 1 : CLASSIFI	CATION AND		<u>GROUPS</u>
	<u>NOMENC</u>	LATURE	Q.10	The C–O–C angle in ether is about
Q.1	Wood spirit is known as –			(A) 180° (B) 190°28'
	(A) Methanol	(B) Ethanol		(C) 110° 105°
	(C) Acetone	(D) Benzene	Q.11	In alcohols, the oxygen of the OH group is attached to a
Q.2	$CH_3OC_2H_5$ is/are known as			carbon by a bond formed by the overlap of a
	(A) ethyl methyl ether	(B) methylethyl ether		hybridised orbital of carbon with a sp <sup>-3</sup> hybridised orbital
0.1	(C) Both (A) and (B)	(D) None of these		of oxygen. (A) sigma: $\operatorname{sp}^2$ (B) sigma: $\operatorname{sp}^3$
Q.3	10 PAC name of m-cresol is	$(\mathbf{D})$ 2 able see b as al		(A) signa, sp <sup>-</sup> (C) $\pi$ : sp <sup>2</sup> (D) $\pi$ : sp <sup>3</sup>
	(A) 3-methylphenol	(B) 3-chlorophenol	0.12	$(D)$ $\pi$ , sp The C-O-H bond angle in alcohols is slightly less than
04	(C) 5-methoxyphenol	(D) benzene-1,5-diol	Q.12	the tetrahedral angles whereas the $C-O-C$ bond angle
Q.4	I monohydric	II. dihydric		in ether is slightly greater because
	III tribydric	IV polyhydric		(A) Of repulsion between the two bulky R groups
	Select an appropriate option	with correct choices		(B) O atom in both alcohols and ether is $sp^3$ , hybridised
	(A) I and II	(B) II and III		(C) Lone pair - lone pair repulsion is greater than bond
	(C) III, IV and I	(D) I, II, III and IV		pair bond pair repulsion
05	IIIPAC name of CIL CIL CI	LCU CU CU is-		(D) None of these
Q.J	TOTAC hand of CH <sub>3</sub> CH <sub>2</sub> CH	$1_2 C \Pi - C \Pi_2 C \Pi_3$ <sup>13</sup>	Q.13	In ethers, the two bond pairs and two lone pairs of
		CH2OH		electrons on oxygen are arranged in a
	(A) 3-propylbutan-1-ol	-		(A) planar arrangement
	(B) 2-ethylpentan-1-ol			(B) tetrahedral arrangement
	(C) 3-methyl hydroxyhexane			(C) trigonal bipyramidal arrangement
	(D) 2-ethyl-2-propyl ethanol			(D) linear arrangement
Q.6	Which is primary alcohol?		PA	<b>RT - 3 : PREPARATION OFALCOHOLS</b>
	(A) Butan-2-ol	(B) Butan-1-ol	Q.14	Ethyl alcohol is industrially prepared from ethylene by
	(C) Propan-2-ol	(D) Isopropyl alcohol		(A) Permanganate oxidation
<b>Q.7</b>	Which of the following alco	hol contains		(B) Catalytic reduction
	$C_{2} = OH$ bond?			(C) Absorbing in $H_2SO_4$ followed by hydrolysis
	sp <sup>3</sup> OII bolid !			(D) Fermentation
	(A) Allylic alcohol	(B) Vinylic alcohol	Q.15	Action of nitrous acid with ethylamine produces
	(C) Phenols	(D) None of these		(A) Ethane (B) Ammonia
Q.8	Give IUPAC name of the cor	npound given :	0.16	(C) Ethyl alcohol (D) Nitroethane
	$CH_3 - CH - CH_2 - CH_2 - CH$	-CH <sub>3</sub>	Q.16	In the commercial manufacture of ethyl alcohol from
		2		starchy substances by fermentation method, which
	$(\Lambda)$ 2 Chlore 5 hydrowithour			(A) Diastase maltase and zymase
	(R) 2-Hydroxy 5-chlorobeys	ine		(B) Maltase, zymase and invertase
	(C) $5$ -Chlorobeyan-2-ol			(C) Diastase zymase and lactase
	(D) 2-Chlorohexan-5-ol			(D) Diastase, invertase and zymase
0.9	Select the incorrect match fr	om the following options.	Q.17	Commercially methanol is prepared by
<b>C</b> <sup>11</sup>	(A) Butan-2-ol $\rightarrow$ sec-butyl	alcohol		(A) Reduction of CO in presence of $ZnO.Cr_2O_3$
	(B) CH CH CH OH $\rightarrow i$	sobutyl alcohol		(B) Methane reacts with water vapours at 900°C in
				presence of Ni catalyst
	CH <sub>3</sub>			(C) Reduction of HCHO by $LiAlH_4$
	(C) $CH_2 - CH - CH_2 \rightarrow gly$	cerol	<u> </u>	(D) Reduction of HCHO by aqueous NaOH
			Q.18	Iertiary butyl alcohol can be prepared by the reaction of
	OH OH OH			(A) Acetaldehyde and ethyl magnesium iodide
	(D) 2-methylpropan-2-ol $\rightarrow$	isobutyl alcohol		(B) Acetone and methyl magnesium iodide
				(C) Formation and propyr magnesium fodide
		-		(D) Butanone and methyl magnesium louide
			246	

**QUESTION BANK** 



- Q.19 Which of the following statement(s) is/are correct about hydroboration- oxidation?
  - (A) Diborane reacts with alkenes to give trialkyl boranes as addition product which is oxidised to alcohol by  $H_2O_2$  in the presence of aqueous NaOH.
  - (B) The alcohol so formed by the addition of water to the alkene by the Markownikoff's rule
  - (C) Alcohol is obtained in the poor yield.
  - (D) All of the above.
- Q.20 Alkenes react with water in the presence of acid as catalyst to form alcohols.

$$CH_3CH = CH_2 + H_2O \xrightarrow{H^+} CH_3 - CH - CH_3$$

The reaction takes place in accordance with

- (A) Hofmann elimination rule
- (B) Saytzeff rule
- (C) Markownikoff's rule
- (D) Anti-Markownikoff's addition
- Q.21 Which of the following compounds on reaction with CH<sub>3</sub>MgBr will give a tertiary alcohol?  $(A)C_6H_5CHO$ (B) C<sub>2</sub>H<sub>5</sub>COOCH<sub>3</sub>  $(C)C_{2}H_{5}COO$ CH<sub>3</sub>

- Q.22 One mole of ethyl acetate on treatment with an excess of  $LiAlH_{A}$  in dry ether and subsequent acidification produces
  - (A) 1 mol acetic acid + 1 mol ethyl alcohol
  - (B) 1 mol ethyl alcohol + 1 mol methyl alcohol
  - (C) 2 moles of ethyl alcohol
  - (D) 1 mol of 2-butanol
- Q.23 The mechanism of the reaction (acid catalysed hydration of alkene) involves the following three steps.
  - I. Nucleophilic attack of water on carbocation.
  - II. Protonation of an alkene to form carbocation by the electrophilic attack of  $H_3O^+$ .
  - III. Deprotonation to form an alcohol.

Identify the sequence for the mechanism of reaction in the acid catalysed hydration of alkenes.

(A) I, II and III (B) II, I and III (C) III, I and II (D) III, II and I

## PART - 4: PHYSICALAND CHEMICAL **PROPERTIES OF ALCOHOLS**

- Q.24 Which statement is not correct about alcohol
  - (A) Alcohol is lighter than water.
  - (B) Alcohol evaporates quickly.
  - (C) Alcohol of less number of carbon atoms is less soluble in water than alcohol of high number of carbon atoms.
  - (D) All of these
- **Q.25** Dehydration of ethanol gives (A) Acetic acid (B) Ethane (C) Ethylene (D) Acetylene
- Q.26 Alcohols of low molecular weight are
  - (A) Soluble in water

- (B) Soluble in all solvents
- (C) Insoluble in all solvents
- (D) Soluble in water on heating
- Q.27 Ethyl alcohol on oxidation with  $K_2Cr_2O_7$  gives (B) Acetaldehyde (A) Acetic acid
  - (C) Formaldehyde (D) Formic acid
- Q.28 The reaction between an alcohol and an acid with the elimination of water molecule is called (A) Esterification (B) Saponification
  - (D) Elimination (C) Etherification
- Q.29 Maximum solubility of alcohol in water is due to (A) Covalent bond (B) Ionic bond (C) H-bond with H<sub>2</sub>O (D) None of the above
- Q.30 When primary alcohol is oxidised with chlorine, it produces (B) CH<sub>2</sub>CHO
  - (A) HCOH (C)CCl<sub>3</sub>CHO
    - $(D)C_3H_7CHO$
- Q.31 Which of the following reagents can not be used to oxidise primary alcohols to aldehydes ? (A)  $CrO_3$  in anhydrous medium
  - (B) KMnO<sub>4</sub> in acidic medium
  - (C) Pyridinium chlorochromate
  - (D) Heat in the presence of Cu at 573 K.
- 0.32 The acidic character of alcohols is due to the (A) non-polar nature of O – H bond (B) polar nature of O - H bond (C) non-polar nature of C - O bond
  - (D) polar nature of C O bond
- Q.33 In the esterification reaction of alcohols (A)  $OH^-$  is replaced by  $C_2H_5OH$ (B) OH<sup>-</sup> is replaced by chlorine (C) H<sup>-</sup> is replaced by sodium metal (D) OH<sup>-</sup> is replaced by CH<sub>3</sub>COO group
- Q.34 Order of esterification of alcohols is (A)  $3^{\circ} > 1^{\circ} > 2^{\circ}$ (B)  $2^{\circ} > 3^{\circ} > 1^{\circ}$ (C)  $1^{\circ} > 2^{\circ} > 3^{\circ}$ (D) None of these
- Q.35 Which of the following alcohols will give the most stable carbocation during dehydration ? (A) 2-Methyl-1-propanol (B) 1-Butanol (C) 2-Methyl-2-propanol (D) 2-Butanol
- Q.36 Arrange the following alcohols in order of increasing reactivity towards sodium metal.
  - (i)  $(CH_2)_2C OH$ (ii) (CH<sub>3</sub>)<sub>2</sub>CH – OH (iii) CH<sub>3</sub>CH<sub>2</sub>OH (A) (iii) < (ii) < (ii)(B)(ii) < (i) < (iii)(C) (i) < (ii) < (iii) (D)(iii) < (i) < (ii)
- Q.37 Identify an appropriate reagent for the conversion of alcohol to carboxylic acid. (A)PCC
  - (B) Anhydrous CrO<sub>3</sub> (D) KMnO<sub>4</sub>/H<sup> $\oplus$ </sup> (C) Cu/573 K
- The process of converting alkyl halides into alcohols 0.38 involves
  - (A) addition reaction
  - (B) substitution reaction
  - (C) dehydrohalogenation reaction
  - (D) rearrangement reaction.



- **Q.39** Acid catalysed dehydration of t-butanol is faster than that of n-butanol because
  - (A) Tertiary carbocation is more stable than primary carbocation
  - (B) Primary carbocation is more stable than tertiary carbocation
  - (C) t-butanol has a higher boiling point
  - (D) Rearrangement takes place during dehydration of tbutanol

#### PART - 5: IDENTIFICATION OF ALCOHOLS

- Q.40 What is the Lucas reagent? (A) Conc.  $HCl + PbCl_2$  (B) Conc.  $HCl + ZnCl_2$ (C) Conc.  $HCl + PbCl_4$  (D) Conc.  $HCl + AlCl_3$
- (C) Conc. HCl+PbCl<sub>4</sub>
   (D) Conc. HCl+AlCl<sub>3</sub>
   Q.41 Methyl alcohol can be distinguished from ethyl alcohol using
  - (A) Fehling solution
  - (B) Schiff's reagent
  - (C) Sodium hydroxide and iodine
  - (D) Phthalein fusion test
- Q.42 Select the correct match of the alcohol with Lucas reagent.
  - (A) Primary alcohol  $\rightarrow$  produces the turbidity immediately.
  - (B) Secondary alcohol → produces the turbidity immediately.
  - (C) Tertiary alcohol  $\rightarrow$  produces the turbidity immediately.
  - (D) All of the above
- **Q.43** Methyl alcohol (methanol), ethyl alcohol (ethanol) and acetone (propanone) were treated with iodine and sodium hydroxide solutions. Which substances will give iodoform test
  - (A) Only ethyl alcohol
  - (B) Only methyl alcohol and ethyl alcohol
  - (C) Only ethyl alcohol and acetone
  - (D) Only acetone
- Q.44 Which of the following compound give yellow precipitate with I<sub>2</sub> and NaOH ? (A) CH<sub>3</sub>CH<sub>2</sub>OH (B) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH (C) C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub> (D) CH<sub>3</sub>OH
- Q.45 Which of the following alcohols reacts most readily with Lucas reagent ?

(A) 
$$CH_3CH_2CH_2OH$$
 (B)  $CH_3 - CH - CH_3$   
 $|$   
 $OH$ 

(C) 
$$CH_3 - C - OH$$
  
 $CH_3 - C - OH$   
 $CH_3 - CH - CH_2OH$   
 $CH_3 - CH - CH_2OH$ 

- Q.46 An unknown alochol is treated with the Lucas reagent to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism
  - (A) secondary alcohol by  $S_N 1$
  - (B) tertiary alcohol by  $S_N 1$
  - (C) secondary alcohol by  $S_{N}2$
  - (D) tertiary alcohol by  $S_N 2^{-1}$

## PART - 6 : USES OF ALCOHOLS

- Q.47 Methylated spirit is (A) Methanol (B) Methanol + ethanol (C) Methanoic acid (D) Methanamide
- Q.48 Denaturation of alcohol is the
  - (A) mixing of CuSO<sub>4</sub> (a foul smelling solid) and pyridine (to give the colour) to make the commercial alcohol unfit for drinking.
  - (B) mixing of CuSO<sub>4</sub> (to give the colour) and pyridine (a foul smelling solid) to make the commercial alcohol unfit for drinking.
  - (C) mixing of  $Cu(OAc)_2$  and ammonia to make the commercial alcohol unfit for drinking.
  - (D) mixing of  $Cu(OAc)_2$  and pyridine to make the commercial alcohol unfit for drinking.
- Q.49 Power alcohol is -
  - (A) An alcohol of 95% purity
  - (B) A mixture of petrol hydrocarbons and ethanol
  - (C) Rectified spirit
  - (D) A mixture of methanol and ethanol
- Q.50 In order to make alcohol undrinkable pyridine and methanol are added to it. The resulting alcohol is called (A) Power alcohol (B) Proof spirit
  - (C) Denatured spirit (D) Poison alcohol

#### **PART - 7 : PREPARATION OF PHENOLS**

Q.51 In the following sequence of reactions,

$$\xrightarrow{\text{Oleum}} P \xrightarrow{(i) \text{ NaOH}} Q$$

- the compound Q formed will be
- (A) Aniline
- (B) Phenol
- (C) Benzaldehyde
- (D) Benzene sulphonic acid
- **Q.52** Cumene on reaction with oxygen followed by hydrolysis gives –

(A) CH<sub>3</sub>OH and C<sub>6</sub>H<sub>5</sub>COCH<sub>3</sub>(B) C<sub>6</sub>H<sub>5</sub>OH and (CH<sub>3</sub>)<sub>2</sub>O (C) C6H<sub>5</sub>OCH<sub>3</sub> and CH<sub>3</sub>OH(D) C<sub>6</sub>H<sub>5</sub>OH & CH<sub>3</sub>COCH<sub>3</sub>

Q.53 Which of the following reactions will not yield phenol?





#### PART - 8 : PHYSICALAND CHEMICAL PROPERTIES OF PHENOLS

- Q.54 For phenol, which of the following statements is correct
  - (A) It is insoluble in water
  - (B) It has lower melting point compared to aromatic
  - hydrocarbons of comparable molecular weight
  - (C) It has higher boiling point than toluene
  - (D) It does not show acidic property
- Q.55 In phenols -
  - (A) OH group is attached in side chain.
  - (B) OH group is directly attached to benzene nucleus.

 $(B)H_2$ 

 $(D)CO_{2}$ 

- (C) Both (A) & (B)
- (D) None
- Q.56 Action of diazomethane on phenol liberates

$$(A)O_2$$

$$(C)N_{2}$$

**Q.57** Which of the following compounds will be most easily attacked by an electrophile ?



- Q.58 Select the incorrect statement about Kolbe's reaction.
  - (A) Phenoxide ion is less reactive than phenol towards electrophilic aromatic substitution.
  - (B) A weak electrophile  $CO_2$  is used in this reaction.
  - (C) ortho-hydroxy benzoic acid is formed as the main product.
  - (D) Salicylic acid is formed as the main product.
- **Q.59** The reaction between phenol and chloroform in the presence of aqueous NaOH is
  - (A) nucleophilic substitution reaction.
  - (B) electrophilic addition reaction.
  - (C) electrophilic substitution reaction.
  - (D) nucleophilic addition reaction.
- **Q.60** Dehydration of the following in increasing order is

(I)
$$\bigcirc$$
 OH(II) $\bigcirc$  OH(III) $\bigcirc$  OH(IV) $\bigcirc$  OH(A) I < II < III < IV(B) II < III < IV < I(C) I < III < IV < II(D) None of thesePhenol is less acidic than(B) o-nitrophenol(A) ethanol(B) onitrophenol

- (C) o-methylphenol (D) o-methoxyphenol.Q.62 Which of the following statement(s) is/are correct?(A) OH group in phenols is more strongly held as
  - compared to OH group in alcohols.(B) OH group in phenols is less strongly held as compared to OH group in alcohols.
  - (C) OH group in phenols is equally strongly held as compared to OH group in alcohols.
  - (D) All of the above

Q.61

**Q.63** Identify the final product of the reaction sequence.

$$\bigcup_{\text{distillation}} Z_n \xrightarrow{\text{CH}_3\text{COCl}} Y$$

(A) Benzophenone

(C) Diphenyl

#### (B) Acetophenone

#### (D) Methyl salicylate

- **Q.64** Salicylic acid can be prepared using Reimer-Tiemann's reaction by treating phenol with
  - (A) Methyl chloride in the presence of anhydrous aluminium chloride.
  - (B) Carbon dioxide under pressure in sodium hydroxide solution.
  - (C) Carbon tetrachloride and concentrated sodium hydroxide.
  - (D) Sodium nitrite and a few drops of concentrated sulphuric acid.

**Q.65** 
$$\rightarrow$$
 + dilute HNO<sub>3</sub>  $\rightarrow$  ?

Select the product(s) formed in the given reaction.



- **Q.66** Ortho-nitrophenol is less soluble in water than p-and mnitrophenols because
  - (A) o-nitrophenol shows intramolecular H-bonding.
  - (B) o-nitrophenol shows intermolecular H-bonding.

(C) melting point of o-nitrophenol is lower than those of m- and p-isomers.

(D) o-nitrophenol is more volatile in steam than those of m- and p-isomers.

**Q.67** Which of the following compounds will react with sodium hydroxide solution in water?

$$\begin{array}{ll} \text{(A)} C_6 H_5 \text{OH} & \text{(B)} C_6 H_5 \text{CH}_2 \text{OH} \\ \text{(C)} (CH_3)_3 \text{COH} & \text{(D)} C_2 H_5 \text{OH} \end{array}$$

- Q.69 For phenol, which of the following statements is correct? (A) It has higher boiling point than toluene
  - (B) It has lower melting point compared to aromatic hydrocarbons of comparable molecular weight
  - (C) It is insoluble in water
  - (D) It does not show acidic property



- Q.70 Phenol when treated with excess of bromine water gives a white precipitate of –
   (A) 2, 4, 6-tribromophenol
   (B) o-bromophenol
  - (C) p-bromophenol (D) bromobenzene
- Q.71 The correct order of strength of acidity of the following compounds is



## PART - 9: USES AND TESTS OF PHENOLS

- Q.73 Phenol can be distinguished from aliphatic alcohol with (A) Tollens reagent (B) Schiff's base (C) FeCl<sub>3</sub> (D) HCl
- Q.74 Choose the correct statement
  - (A) Some phenols can be used as flavouring agents.
  - (B) Some phenols can be used as perfumes.
  - (C) Vanillin (present in oil of vanilla bean) is an example of phenol used as a flavouring agents.
  - (D) All of these
- Q.75 Choose the correct statement -
  - (A) Phenol give deep blue or violet colour with neutral FeCl<sub>3</sub>.
  - (B) Phenol give liebermann's nitroso reaction.
  - (C) Phenol produces white precipitate of
  - 2,4, 6 tribromophenol with bromine water. (D) All of these

#### PART - 10 : PREPARATION OF ETHERS

Q.76 The reaction given below is known as

 $C_2H_5ONa + IC_2H_5 \longrightarrow C_2H_5OC_2H_5 + NaI$ 

- (A) Kolbe's synthesis (B) Wurtz's synthesis
- (C) Williamson's synthesis (D) Grignard's synthesis
- **Q.77** The reagent used for the preparation of higher ether from halogenated ethers is
  - (A) conc.  $H_2SO_4$  (B) Sodium alkoxide
  - (C) Dry silver oxide (D) Grignard reagent

Q.78 In which case methyl-t-butyl ether is formed –

$$(A)(C_2H_5)_3CONa + CH_3Cl(B)(CH_3)_3CONa + CH_3Cl$$

(C)  $(CH_3)_3CONa + C_2H_5Cl$  (D)  $(CH_3)_2CONa + CH_3Cl$ 

Q.79 Ethers are prepared by the reaction of sodium alkoxides and alkyl halides. Which of the following reagents should be taken to prepare methyl tert-butyl ether? (A)  $(CH_3)_3C-Br+NaOCH_3$ (B)  $CH_3Br+NaOC(CH_3)_3$ 

- $(C) CH_3 CH_2 Br + NaOC(CH_3)_2$
- $(D) (CH_3)_2 \tilde{C} Br + NaOCH_2 \tilde{C}H_3$
- **Q.80** is an important method for the preparation of symmetrical and unsymmetrical ethers.
  - (A) Williamson's synthesis
  - (B) Riemer-Tiemann reaction
  - (C) Kolbe's reaction(D) None of these
- **Q.81** Ether is obtained from ethyl alcohol in presence of  $H_2SO_4$  at

(A)113K	(B)443K
(C)413 K	(D) 213 K

**Q.82** An equimolar quantities of ethanol and propanol is heated with cone,  $H_2SO_4$ , The product formed is/are (A)  $C_2H_5OC_2H_5$  (B)  $C_3H_7OC_3H_7$ (C)  $C_2H_5OC_3H_7$  (D) All of these

#### PART - 11 : PHYSICALAND CHEMICAL PROPERTIES OF ETHERS

- Q.83 According to Lewis concept of acids and bases, ether is (A) Acidic (B) Basic
- (C) Neutral (D) AmphotericQ.84 An ether is more volatile than an alcohol having the same molecular formula. This is due to
  - (A) Dipolar character of ethers
  - (B) Alcohols having resonance structures
  - (C) Inter-molecular hydrogen bonding in ethers
  - (D) Inter-molecular hydrogen bonding in alcohols
- **Q.85** Which of the following product is formed, when ether is exposed to air

(A) Oxide	(B) Alkanes
(C) Alkenes	(D) Peroxide of diethyl ether

- **Q.86** The ether that undergoes electrophilic substitution reaction is
  - $\begin{array}{ccc} (A) CH_3OC_2H_5 \\ (C) CH_3OCH_3 \end{array} \qquad \begin{array}{ccc} (B) C_6H_5OCH_3 \\ (D) C_2H_5OC_2H_5 \end{array}$
- **Q.87** Ethers have lower boiling points than their corresponding isomeric alcohols because of

(A) hydrogen bonding in alcohols that is absent in ethers due to low polarity.

- (B) hydrogen bonding in ethers due to high polarity.
- (C) insolubility of ethers in water due to less polarity.
- (D) inertness of ethers as compared to alcohols.
- Q.88 Ethers have a net dipole moment because
  - (A) C O bonds in ethers are non-polar.
  - (B) C O bonds in ethers are polar.
  - (C) C C bonds in ethers are polar.
  - (D) C C bonds in ethers are non-polar.
- **Q.89** The large difference in the boiling points of alcohols and ethers is due to the presence of
  - (A) van der Waals' forces in alcohols.
  - (B) dipole-dipole interaction in alcohols.
  - (C) hydrogen bonding in alcohols.
  - (D) ion-ion interaction in alcohols.



#### EXERCISE - 2 [LEVEL-2]

#### Choose one correct response for each question.

Q.1	Coconut oil upon alka	aline hydrolysis gives –
	(A) Glycol	(B) Alcohol
	(C) Glycerol	(D) Ethylene oxide
0.2	Which enzyme conve	rts glucose and fructose bo

Q.2	Which enzyme conve	erts glucose and fructose both into
	ethanol	
	(A) Diastase	(B) Invertase

- (C) Zymase (D) Maltase Q.3 Salicylaldehyde can be prepared from (A) Phenol and chloroform
  - (B) Phenol, chloroform and sodium hydroxide
  - (C) Phenol, carbon tetrachloride and NaOH

- Q.4 Acetone on treatment with  $CH_3 Mg I$  and on further hydrolysis gives
  - (A) Isopropyl alcohol (B) Primary alcohol
  - (C) Acetic acid (D) 2-Methylpropan-2-ol

(B) C<sub>2</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>OH

 $(D) \overline{C_2}H_5CHO$ 

**Q.5** In the following reaction 'A' is

$$C_2H_5MgBr + H_2C - CH_2 \xrightarrow{H_2O} A$$

 $(A) C_2 H_5 CH_2 CHO$  $(C) C_2 H_5 CH_2 OH$ 

- Q.6 In Williamson's synthesis, ethoxyethane is prepared by
  (A) Passing ethanol over heated alumina
  (B) Sodium ethoxide with ethyl bromide
  (C) Ethyl alcohol with sulphuric acid
  - (D) Ethyl iodide and dry silver oxide
- Q.7 Formation of diethyl ether from ethanol is based on a (A) Dehydration reaction
  - (B) Dehydrogenation reaction
  - (C) Hydrogenation reaction
  - (D) Heterolytic fission reaction

Q.8 
$$C_6H_5 - CH = CHCHO \xrightarrow{X} C_6H_5CH = CHCH_2OH$$
.  
In the above sequence X can be  
(A)  $H_2/Ni$  (B) NaBH<sub>4</sub>  
(C)  $K_2Cr_2O_7/H^+$  (D) Both (A) and (B)  
Q.9 Methylphenyl ether can be obtained by reacting  
(A) Phenoleta ions and methyl iodida

- (A) Phenolate ions and methyl iodide(B) Methoxide ions and bromobenzene
  - (C) Methanol and phenol
- (D) Bromo benzene and methyl bromide
- $\begin{array}{ccc} \textbf{Q.10} & 23 \text{ g of Na will react with methyl alcohol to give} \\ (A) \text{ One mole of oxygen} & (B) \text{ One mole of H}_2 \\ (C) 1/2 \text{ mole of H}_2 & (D) \text{ None of these} \end{array}$
- Q.11 Which reagent is useful in converting 1-butanol to 1-bromobutane.(A) CHBr<sub>3</sub>(B) Br<sub>2</sub>
  - $\begin{array}{c} (C) CH_3Br \\ (D) PBr_3 \end{array}$
- **Q.12** Which of the following gives ketone on oxidation (A)  $(CH_3)_3COH$  (B)  $CH_3CH_2CH_2OH$ (C)  $(CH_3)_2CHCH_2OH$  (D)  $CH_3CHOHCH_3$

[LLE										
Q.13	Which of the following com	pounds is oxidised to prepare								
	methyl ethyl ketone									
	(A) 2 - propanol	(B) 1 - butanol								
	(C) 2 - butanol (D) Tert-butyl alco									
Q.14	Isopropyl alcohol heated a to form	t 300°C with copper catalyst								
	(A) Acetone	(B) Dimethyl ether								
	(C) Acetaldehyde	(D) Ethane								
0.15	Glycerol is a –	(2) 2000								
<b>L</b>	(A) Primary alcohol	(B) Monohydric alcohol								
	(C)Secondary alcohol	(D) Trihydric alcohol								
Q.16	Glycerine has –									
-	(A) One primary and two se	econdary –OH groups.								
	(B) One secondary and two	primary –OH groups.								
	(C) Three primary – OH gr	oups.								
	(D) Three secondary – OH	groups.								
Q.17	RMgBr on reaction with a	n excess of oxygen followed								
	by hydrolysis gives –									
	(A) RH	(B) ROOR								
	(C) ROOH	(D) ROH								
Q.18	Which compound is forme	ed when CH <sub>3</sub> OH reacts with								
	$CH_3 - Mg - X.$									
	(A) Acetone	(B) Alcohol								
	(C) Methane	(D) Ethane								
Q.19	Glycerol reacts with $P_4 + I_2$	<sub>2</sub> to form –								
	(A) Aldehyde	(B) Allyl iodide								
<b>•••</b>	(C) Allyl alcohol	(D) Acetylene								
Q.20	The reagent which easil	y reacts with ethanol and								
	propanol is	(D) Crignand and goat								
	(A) Fenting solution	(B) Grignard reagent								
0 21	(C) Schill Steagent When venour of otherol	(D) Ionen's reagent								
Q.21	ashestos in excess of air th	are passed over platinised								
	$(\Delta)$ CH CHO	(B) CH COCH								
	$(\Gamma)$ C H.	$(D) CH_2COOH$								
0.22	Which of the following is t	the most suitable method for								
~	removing the traces of wat	er from ethanol								
	(A) Heating with Na metal.									
	(B) Passing dry HCl through	zh it								
	(C) Distilling it									
	(D) Reacting with Mg									
Q.23	Conc. $H_2SO_4$ heated with ex	xcess of C <sub>2</sub> H <sub>5</sub> OH at 140°C to								
	form	2 5								
	$(A) CH_3 CH_2 - O - CH_3$									
	$(B) CH_3 CH_2 - O - CH_2 CH$	3								
	$(C) CH_3 - O - CH_2 - CH_2 - CH_2$	-CH <sub>3</sub>								
	$(D) CH_2 = CH_2$	5								
Q.24	Methanol & ethanol are mi	scible in water due to								
	(A) Covalent character									
	(B) Hydrogen bonding cha	racter								
	(C) Oxygen bonding charac	cter								
	(D) None of these									

Q.25 Amongst the following, HBr reacts fastest with– (A) Propane-1-ol (B) Propane-2-ol (C) 2-methyl propan-1-ol (D) 2-methyl propan-2-ol



- Q.26 Aspirin is also known as (A) Methyl salicylic acid (B) Acetyl salicylic acid (C) Acetyl salicylate (D) Methyl salicylate
- Q.27 The compound with the highest boiling point is (B) CH<sub>2</sub>OH  $(A) CH_4$  $(C) CH_{3}Cl$ 
  - $(D) CH_3Br$
- Q.28 A mixture of methanol vapours and air is passed over heated copper. The products are
  - (A) Carbon monoxide and hydrogen.
  - (B) Formaldehyde and water vapour.
  - (C) Formic acid and water vapour.
  - (D) Carbon monoxide and water vapour.
- Q.29 In the following reaction

$C_2H_5OC_2H_5 + 4[H] - Re$	$\xrightarrow{\text{d P+HI}} 2X + H_2O$ , X is
-----------------------------	--

- Q.30 Diethyl ether absorbs oxygen to form
- (A) Red coloured sweet smelling compound.
  - (B) Acetic acid.
  - (C) Ether suboxide.
  - (D) Ether peroxide.
- Q.31 The boiling point of methanol is greater than that of methyl thiol because
  - (A) There is intramolecular hydrogen bonding in methanol and intermolecular hydrogen bonding in methyl thiol.
  - (B) There is intermolecular hydrogen bonding in methanol and no hydrogen bonding in methyl thiol.
  - (C) There is no hydrogen bonding in methanol and intermolecular hydrogen bonding in methyl thiol.
  - (D) There is intramolecular hydrogen bonding in methanol and no hydrogen bonding in methyl thiol.
- Q.32 With anhydrous zinc chloride, ethylene glycol gives (A) Formaldehyde (B) Acetylene (C) Acetaldehyde (D) Acetone
- Q.33 Which of the following compound give yellow precipitate with I2 and NaOH  $(A) CH_2 OH$ (B) CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH
  - $(D) CH_3 CH_2 OH$  $(C)C_{2}H_{5}OC_{2}H_{5}$
- Q.34 On reaction with hot conc.  $H_2SO_4$ , which one of the following compounds loses a molecule of water (A) CH<sub>3</sub>COCH<sub>3</sub> (B) CH<sub>3</sub>COOH  $(C) CH_3 OCH_3$ (D) CH<sub>3</sub>CH<sub>2</sub>OH
- Q.35 The best reagent to convert pent-3-en-2-ol into pent-3en-2-one is
  - (A) acidic permanganate
  - (B) acidic dichromate
  - (C) chromic anhydride in glacial acetic acid
  - (D) pyridinium chlorochromate.
- Q.36 Which of the following alcohols gives the best yield of dialkyl ether acid?
  - (A) 2-Pentanol (B)2-Methyl-2-butanol
  - (C) 1-Pentanol (D) 2-Propanol
- Q.37 The major product of acid catalysed dehydration of 2-methylcyclohexanol and butan-l-ol are respectively (A) 1-methylcyclohexene and but-l-ene

- (B) 2-methylcyclohexene and but-2-ene
- (C) 2-methylcyclohexene and butane
- (D) 1-methylcyclohexene and but-2-ene.
- **Q.38** Correct order of boiling points among following: CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub>, CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>OH

$$\begin{array}{cccc} (X) & (Y) & (Y) & (Z) \\ (A) & X > Y > Z & (B) & Y > X > Z \end{array}$$

- (C) Z > X > Y(D) Z > Y > X
- Q.39 I. Methanol is a colourless liquid and highly poisonous in nature.
  - II. Ingestion of small quantities of methanol can cause blindness and large quantities causes the death.
  - III. Methanol is used as a solvent in paints varnishes and chiefly for making formaldehyde.

Which of the following statement(s) is/are correct? (A) Only I (B) Only II

- Q.40 The correct sequence of decreasing acidity is (A)  $(CH_3)_3COH > (CH_3)_3CHOH > C_3H_5OH > CH_3OH$ (B)  $CH_{2}OH > C_{2}H_{5}OH > (CH_{2})_{2}CHOH > (CH_{2})_{3}COH$ (C)  $C_2H_5OH > CH_3OH > (CH_3)_3COH > (CH_3)_2CHOH$ (D)  $(CH_3)_2CHOH > (CH_3)_3COH > C_2H_5OH > CH_3OH$
- 0.41 The best method to prepare 3-methylbutan-2-ol from 3-methylbut-1-ene is (A) Addition of water in presence of dil.  $H_2SO_4$ (B) Addition of HCl followed by reaction with dil. NaOH (C) Hydroboration - oxidation reaction (D) Reimer - Tiemann reaction.
- Q.42 Picric acid is a yellow coloured compound. Its chemical name is -

Q.43 An organic compound with molecular formula  $C_4H_{10}O$ does not react with sodium. With excess of HI it gives only one type of alkyl halide. The compound is -

(A) 
$$C_2H_5OC_2H_5$$
 (B)  $CH_3CHCH_3$ 

OCH<sub>3</sub> (D) CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH (C)  $CH_3CH_2CH_2OCH_3$ 

Q.44 Which of the following alcohols is dehydrated most easily with conc.  $H_2SO_4$ ?

 $(A) p-O_2NC_6H_4CH(OH)CH_3 (B) p-ClC_6H_4CH(OH)CH_3$ (C) p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CH(OH)CH<sub>3</sub> (D) C<sub>6</sub>H<sub>5</sub>CH(OH)CH<sub>3</sub>

- Q.45 Aspirin
  - (A) is formed by the acetylation of phenolic carboxylic acid.
  - (B) possesses analgesic, antiinflammatory & antipyretic properties.
  - (C) Both (A) and (B)
  - (D) None of the above
- **Q.46** Anisole on reaction with chloromethane in presence of anhydrous AlCl<sub>3</sub> gives
  - (A) o-methyl anisole and p-methoxy anisole
  - (B) p-methyl anisole and p-methoxy anisole
  - (C) o-methyl anisole and p-methyl anisole
  - (D)o-methoxy acetophenone & p-methoxy acetophenone

**QUESTION BANK** 



- Q.47 Unlike phenol, 2,4-dinitrophenol is soluble in sodium carbonate solution in water because -
  - (A) presence of two  $-NO_2$ , groups in the ring makes 2, 4-dinitrophenol a stronger acid than phenol.
  - (B) presence of two  $-NO_2$  groups in the ring makes 2, 4-dinitrophenol a weaker acid than phenol.
  - (C) presence of two  $-NO_2$  groups make the hydrogen bonding easier, making 2, 4-dinitrophenol soluble.
  - (D) nitro group reacts with  $Na_2CO_3$  while OH group does not.
- Q.48 Out of 2-chloroethanol and ethanol which is more acidic and why?
  - (A) 2-Chloroethanol due to + I-effect of Cl
  - (B) Ethanol due to + I-effect of CH<sub>2</sub>
  - (C) 2-Chloroethanol due to I-effect of Cl
  - (D) Ethanol due to -I-effect of CH<sub>2</sub>
- Q.49 Compound  $C_2H_6O$  has two isomers X and Y. On reaction wth HI, X gives alkyl iodide and water while Y gives alkyl iodide and alcohol. Compounds X and Y are respectively -

(A) C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub> and CH<sub>3</sub>OC<sub>2</sub>H<sub>5</sub> (B) CH<sub>3</sub>OCH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub>OCH<sub>3</sub> (C) C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>OCH<sub>3</sub>

$$(D) CH_2OH and CH_2OCH_2$$

Q.50 An oxygen containing organic compound upon oxidation forms a carboxylic acid as the only organic product with its molecular mass higher by 14 units. The organic compound is -

(A) a primary alcohol (B) an aldehyde

(C) a ketone (D) a secondary alcohol Q.51 The compound which gives turbidity immediately with Lucas reagent at room temperature is -

> (A) butan-2-ol (B) butan-1-ol

- (C) 2-methyl propan-1-ol (D) 2-methyl propan-2-ol Q.52 The conversion of m-nitrophenol to resorcinol involves respectively
  - (A) diazotization, reduction and hydrolysis
  - (B) hydrolysis, diazotization and reduction
  - (C) reduction, diazotization and hydrolysis
  - (D) hydrolysis, reduction and diazotization
- Q.53 Power alcohol is a mixture of (A) 80% Petrol+20% Benzene+Small quantity of Ethanol (B) 80% Petrol + 20% Ethanol + Small quantity of Benzene (C) 80% Ethanol + 20% Benzene+ Small quantity of Petrol (D) 50% Petrol + 50% Ethanol+ Small quantity of Benzene Q.54 Identify C in the following

(A) Water

(D) Cumene hydroperoxide (C) Propanone

Q.55 0.44 g of a monohydric alcohol when added to methylmagnesium iodide in ether liberates at S.T.P., 112cm<sup>3</sup> of methane. With PCC the same alcohol forms a carbonyl compound that answers silver mirror test. The monohydria alaahal is



(A) 
$$CH_3CH_2CH_2CH_2OH$$
 (B)  $CH_3 - CHCH_2OH$ 

CH<sub>3</sub>

(C)  $HOH_2C - CH_2OH$ (D) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>OH

Q.59 Ethanol is heated with concentrated  $H_2SO_4$ . The product formed is -

(A) 
$$CH_3 - C - O - C_2H_5$$
 (B)  $C_2H_6$ 

(C) 
$$C_2H_4$$
 (D)  $C_2H_2$   
LiAlH<sub>4</sub> converts acetic acid into –  
(A) Acetaldehyde (B) Methane  
(C) Ethyl alcohol (D) Methyl alcohol  
**Q.61** The increasing order of boiling points of

$$\begin{array}{c} 1^{\circ}, 2^{\circ}, 3^{\circ} \text{ alcohol is} - \\ (A) \ 1^{\circ} > 2^{\circ} > 3^{\circ} \\ (C) \ 2^{\circ} > 1^{\circ} > 3^{\circ} \\ (D) \text{ None} \end{array}$$

- Q.62 Solubility of lower alcohols in water is due to (A) Formation of hydrogen bond between alcohol and water molecules.
  - (B) Hydrophobic nature of alcohol.
  - (C) Increases in boiling points
  - (D) None of these



**Q.63** Dow's process used in the industrial preparation of phenol, is

(A) 
$$C_6H_5Cl \xrightarrow{\text{NaOH}} C_6H_5OH + \text{NaCH}$$

(B) 
$$C_6H_5Cl + H_2O \xrightarrow{SO_2}{425^{\circ}C} C_6H_5OH + HCl$$

- (C)  $C_6H_5NH_2 + HNO_2 \xrightarrow{\Delta} C_6H_5OH + N_2 + H_2O$
- (D)  $C_6H_5N_2Cl + H_2O \rightarrow C_6H_5OH + N_2 + HCl$
- Q.64 Which of the following is not a phenolic compound (A) Salol (B) o-Cresol (C) Anisole (D) Quinol
- Q.65 Unacceptable name for a compound containing one OH group attached to benzene nucleus would be -(A) Carbolic acid (B) Hydroxybenzene (C) Catechol (D) Phenol **Q.66** How many  $\pi$  electrons are there in a planar ring of phenol (A) 4 (B)6 (C) 8 (D)10 Q.67 Anhydrides of alcohol are nothing but (A) Ethers (B) Aldehydes (C) Esters (D) Alkyl anhydrides Q.68 Diethyl ether acts as a -
  - (A) Lewis acid(C) Reducing agent
- (B) Lewis base(D) Oxidising agent

#### **EXERCISE - 3 (NUMERICAL VALUE BASED QUESTIONS)**

**Q.7** 

#### NOTE : The answer to each question is a NUMERICAL VALUE.

Q.1 If IUPAC name of the compound

$$\begin{array}{c} & CH_3 \\ H_3 - CH - CH - CH - C - CH_3 \\ | & | \\ CH_3 & OH \end{array} \begin{array}{c} is: \\ CH_3 \end{array}$$

X, 2, 4-trimethylpentan-3-ol. Find the value of X.

**Q.2** If IUPAC name of the compound

$$CH_3O - CH_2 - CH - CH_3$$
 is:  
 $|$   
 $CH_3$ 

X-methoxy-2-methylpropane. Find the value of X.

**Q.3** IUPAC name of aspirin is : X-acetoxybenzoic acid. Find the value of X.

#### For Q.4-Q.6

(i) 
$$CH_3 - C - CH_2OH$$
  
(i)  $CH_3 - C - CH_2OH$   
(ii)  $H_2C = CH - CH_2OH$   
(iii)  $CH_3 - CH_2 - CH_2 - OH$ 



Q.4 Number of primary alcohols in above structures are –

Q.5 Number of secondary alcohols in above structures are –

Q.6 Number of tertiary alcohols in above structures are –

$$\begin{array}{c} \mathrm{CH}_3-\mathrm{C=CH-C=CH-C=CH-C=CH_3}\\ \mathrm{I} & \mathrm{I} & \mathrm{I} & \mathrm{I} \\ \mathrm{CH}_3 & \mathrm{CH}_3 & \mathrm{CH}_3 & \mathrm{CH}_3 & \mathrm{O} \end{array}$$

Find (X + Y - Z) for the above given product which is formed by aldol condensation :

- X = total products (including stereoisomers)
- Y = Number of acetone molecules used in the reaction
- Z = Number of aldol condensation reaction.



#### **EXERCISE - 4 [PREVIOUS YEARS JEE MAIN QUESTIONS]**

Q.1 Maximum dehydration takes place that of [AIEEE 2002]



- Q.2 An ether is more volatile than alcohol having the same molecular formula. This is due to [AIEEE 2003]
  (A) Inter molecular hydrogen bonding in ethers
  (B) Inter molecular hydrogen bonding in alcohols
  (C) Dipolar character of ethers
  (D) Alcohols having resonance structures
- Q.3 When  $CH_2 = CH COOH$  is reduced with LiAlH<sub>4</sub>, the compound obtained will be [AIEEE 2003] (A)  $CH_3 - CH_2 - CH_2OH$  (B)  $CH_3 - CH_2 - CHO$ (C)  $CH_3 - CH_2 - COOH$  (D)  $CH_2 = CH - CH_2OH$
- (A) Ethyl acetate (B) Acetic acid
  (C) Acetamide (D) Butane-2-one
  Q.6 Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the
  - corresponding alcohol and acid ?[AIEEE 2004](A) Phenol(B) Benzaldehyde(C) Butanal(D) Benzoic acid
- Q.7 Among the following compounds which can be dehydrated very easily is [AIEEE 2004]

$$(A) CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}OH(B) CH_{3}CH_{2}CH_{2}CH_{2}CH CH_{3}$$

$$CH_{3}$$

$$(C) CH_{3}CH_{2}CCH_{2}CH_{3} (D) CH_{3}CH_{2}CH CH_{2}CH_{2}OH$$

$$O$$

$$CH_{3}$$

Q.8 p-cresol reacts with chloroform in alkaline medium to give the compound A which adds hydrogen cyanide to form, the compound. B The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is - [AIEEE-2005]



**Q.9** HBr reacts with  $CH_2 = CH - OCH_3$  under anhydrous conditions at room temperature to give - [AIEEE 2006] (A) BrCH<sub>2</sub>CHO and CH<sub>3</sub>OH (B) BrCH<sub>2</sub>-CH<sub>2</sub>-OCH<sub>3</sub> (C) H<sub>3</sub>C-CHBr-OCH<sub>3</sub> (D) CH<sub>3</sub>CHO and CH<sub>3</sub>Br

Q.10 
$$\bigcirc^{\text{OH}}_{\text{+} \text{CHCl}_3 + \text{NaOH}} \rightarrow \bigcirc^{\text{ONa}}_{\text{CHO}}$$
.

The electrophile involved in the above reaction is - (A) dichlorocarbene (:CCl<sub>2</sub>) [AIEEE 2006]

(B) trichloromethyl anion ( $\overset{\diamond}{\text{CCl}}_3$ )

(C) formyl cation (
$$\stackrel{\oplus}{CHO}$$
)

- (D) dichloromethyl cation ( $CHCl_2$ )
- Q.11 The structure of the compound that gives a tribromo derivative on treatment with bromine water is -

[AIEEE 2006]



Q.12 In the following sequence of reactions,  $CH_3CH_2OH$ 

$$\xrightarrow{P+I_2} A \xrightarrow{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D,$$
then compound 'D' is- [AIEEE 2007]
(A) butanal (B) n-butyl alcohol
(C) n-propyl alcohol (D) propanal
Phenol, when it first reacts with concentrated sulphuric
acid and then with concentrated nitric acid, gives -
[AIEEE 2008]

(A) o-nitrophenol	(B) p-nitrophenol
(C) nitrobenzene	(D) 2,4,6-trinitrobenzene

Q.13



Q.14 The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is [AIEEE 2009]

		[AIEEE 2009]
	(A) salicylaldehyde	(B) salicyclic acid
	(C) phthalic acid	(D) benzoic acid
Q.15	From amongst the follow	ing alcohols the one that would
	react fastest with conc. H	ICl and anhydrous ZnCl <sub>2</sub> , is

- [AIEEE 2010] (A) 2-Butanol (B) 2-Methylpropan-2-ol
- (C) 2-Methylpropanol (D) 1-Butanol
- Q.16 The main product of the following reaction is

$$C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{Conc. H_2SO_4}$$



- Q.17 Phenol is heated with a solution of mixture of KBr and KBrO<sub>3</sub>. The major product obtained in the above reaction is : [AIEEE 2011] (A) 2-Bromophenol (B) 3-Bromophenol
  - (C) 4-Bromophenol (D)2, 4, 6 Tribromophenol
- **Q.18** Which of the following reagents may be used to distinguish between phenol and benzoic acid ?

	[AIEEE 2011]
(B) Tollen's	reagent

(A) Aqueous NaOH(C) Molisch reagent

(B) Tollen's reagent	
(D) Neutral FeCl <sub>3</sub>	

- Q.19 Trichloroacetaldehyde was subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another compound. The other compound is [AIEEE 2011]
  (A) 2, 2, 2-Trichloroethanol (B) Trichloromethanol
  (C) 2, 2, 2-Trichloropropanol (D) Chloroform
- Q.20 Ortho-Nitrophenol is less soluble in water than p- and m- Nitrophenols because : [AIEEE 2012]
   (A) o-Nitrophenol is more volatile steam than those of m- and p-isomers.
  - (B) o-Nitrophenol shows Intramolecular H-bonding
  - (C) o-Nitrophenol shows intermolecular H-bonding
  - (D) Melting point of o-Nitrophenol is lower than those of m- and p-isomers.
- Q.21 Iodoform can be prepared from all except [AIEEE 2012] (A) Ethyl methyl ketone (B) Isopropyl alcohol (C) 3-Methyl-2-butanone (D) Isobutyl alcohol
- Q.22 In the given transformation, which the following is the most appropriate reagent ? [AIEEE-2012]



- Q.23 An unknown alochol is treated with the Lucas reagent to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism – [JEE MAIN 2013]
  - (A) secondary alcohol by  $S_N l$
  - (B) tertiary alcohol by  $S_N 1$
  - (C) secondary alcohol by  $S_N 2$
  - (D) tertiary alcohol by  $S_N^2$
- Q.24 Sodium phenoxide when heated with CO<sub>2</sub> under pressure at 125°C yields a product which on acetylation produces C. [JEE MAIN 2014]

$$\bigcirc \overset{\text{ONa}}{\longrightarrow} + \text{CO}_2 \xrightarrow{125^{\circ}\text{C}}{5 \text{ atm}} \text{B} \xrightarrow{\text{H}^+}{\text{Ac}_2\text{O}} \text{C}$$

The major product C would be:



- Q.25 The most suitable reagent for the conversion of  $R-CH_2-OH \rightarrow R-CHO \text{ is} -$  [JEE MAIN 2014] (A) CrO<sub>3</sub> (B) PCC (Pyridinium Chlorochromate) (C) KMnO<sub>4</sub> (D) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>
- Q.26 The product of the reaction given below is:





**Q.27** Phenol reacts with methyl chloroformate in the presence of NaOH to form product A. A reacts with Br<sub>2</sub> to form product B. A and B are respectively: [JEE MAIN 2018]



256





Q.28 The major product formed in the following reaction is :



**Q.29** Phenol on treatment with  $CO_2$  in the presence of NaOH followed by acidification produces compound X as the major product. X on treatment with (CH<sub>2</sub>CO)<sub>2</sub>O in the presence of catalytic amount of H<sub>2</sub>SO<sub>4</sub> produces :

[**JEE MAIN 2018**]



Q.30 The product formed in the reaction of cumene with  $O_2$ followed by treatment with dil. HCl are :

[JEE MAIN 2019 (Jan)]



An organic compound 'X' showing the following Q.31 solubility profile is -[JEE MAIN 2019 (April)]



(B) Oleic acid

Q.32

(D) Benzamide

An organic compound neither reacts with neutral ferric chloride solution nor with Fehling solution, It however, reacts with Grignard reagent and gives positive iodoform test. The compound is

[JEE MAIN 2019 (April)]









1-methyl ethylene oxide when treated with an excess of Q.34 HBr produces : [**JEE MAIN 2020 (JAN)**]



- Q.35 A solution of m-chloroaniline, m-chlorophenol and mchlorobenzoic acid in ethyl acetate was extracted initially with a saturated solution of NaHCO<sub>3</sub> to give fraction A. The left over organic phase was extracted with dilute NaOH solution to give fraction B. The final organic layer was labelled as fraction C. Fractions A, B and C, contain respectively : [**JEE MAIN 2020 (JAN)**]
  - (A) m-chlorobenzoic acid, m-chloroaniline and m-chlorophenol.
  - (B) m-chloroaniline, m-chlorobenzoic acid and m-chlorophenol.



(C) c > b > a

- (C) m-chlorobenzoic acid, m-chlorophenol and m-chloroaniline.
- (D) m-chlorophenol, m-chlorobenzoic acid and m-chloroaniline.
- Q.36 Stability order of following alkoxide ions is



(A) c > b > a	

òн

(D)

(b) (c) [JEE MAIN 2020 (JAN)] (B) a > c > b(D) c > a > b

OH

OH

OH

(C) b > a > c (D) c > a > bQ.37 Major product in the following reaction is

юн

ОН



dil. H<sub>2</sub>SO<sub>4</sub>



(D) b > c > a

**Q.39** There are two compounds A and B of molecular formula  $C_9H_{18}O_3$ . A has higher boiling point than B. What are the possible structures of A and B?

[JEE MAIN 2020 (JAN)]







259



[AIPMT 2015]

(A) 
$$CH_2 = C - CH_2 - CH_3$$
 and  $CH_2 - CH_2 - CH_3$   
Br

(B) 
$$CH_2 = \overset{CH_3}{\overset{}_{\text{CH}_2} - CH_2 - CH_3} \text{ and } \overset{CH_3}{\underset{\text{Br}}{\overset{}_{\text{CH}_2} - CH_2 - CH_2 - CH_3}}$$

(C) 
$$CH_3 \xrightarrow[]{CH_3} CH_3$$
  
(C)  $CH_3 - C = CH - CH_3$  and  $CH_3 - C - CH_2 - CH_3$   
 $H_{Br}$ 

(D) 
$$CH_3 \xrightarrow{CH_3} H_3$$
  
(D)  $CH_3 - C = CH - CH_3$  and  $CH_3 - CH - CH - CH_3$   
Br

Q.15 In the following sequence of reactions

$$CH_3 - Br \xrightarrow{KCN} A \xrightarrow{H_3O^+} B \xrightarrow{LiAlH_4} C,$$
  
the end product (C) is : [AIPMT (PRE) 2012]  
(A) Acetone (B) Methane  
(C) Acetaldehyde (D) Ethyl alcohol  
Which of the following compounds can be used as an

**Q.16** Which of the following compounds can be used as antifreeze in automobile radiators ?

Q.17 Among the following ethers, which one will produce methyl alcohol on treatement with hot concentrated HI?

(A) 
$$CH_3 - CH - CH_2 - O - CH_3$$
 [NEET 2013]  
(B)  $CH_3 - CH_2 - CH_2 - CH_2 - O - CH_3$   
(C)  $CH_3 - CH_2 - CH - O - CH_3$  (D)  $CH_3 - CH_3 - CH_3$   
(C)  $CH_3 - CH_2 - CH - O - CH_3$  (D)  $CH_3 - CH_3 - CH_3$   
(C)  $CH_3 - CH_2 - CH - O - CH_3$  (D)  $CH_3 - CH_3 - CH_3$ 

- Q.18Among the following sets of reactants which one<br/>produces anisole?[AIPMT 2014](A)  $CH_3CHO; RMgX$ <br/>(B)  $C_6H_5OH; NaOH; CH_3I$ <br/>(C)  $C_6H_5OH; neutral FeCl_3$ <br/>(D)  $C_6H_5-CH_3; CH_3COCI; AICl_3$ Q.19Q.19Which of the following will not be soluble in sodium
- hydrogen carbonate? [AIPMT 2014] (A) 2,4,6-trinitrophenol (C) o-Nitrophenol (D) Benzenesulphonic acid

$$\begin{array}{c} CH_3 \\ CH_3 - C \\ - ONa + CH_3CH_2Cl \longrightarrow CH_2 - CH_2 - OH_2 - CH_3 \\ CH_3 \\ CH_3 \end{array} \rightarrow \begin{array}{c} CH_3 \\ - OH_2 - OH_2 - OH_2 - OH_3 \\ - OH_3 - OH_3 - OH_3 \\ - OH_3 - OH_3 - OH_3 \\ - OH_3 - OH_3 - OH_3 - OH_3 \\ - OH_3 - OH_3 - OH_3 - OH_3 \\ - OH_3 - OH_3 - OH_3 - OH_3 \\ - OH_3 - OH_3 - OH_3 - OH_3 \\ - OH_3 - OH_3 - OH_3 - OH_3 \\ - OH_3 - OH_3 - OH_3 - OH_3 \\ - OH_3 - OH_3 - OH_3 - OH_3 \\ - OH_3 - OH_3 - OH_3 - OH_3 \\ - OH_3 - OH_3 - OH_3 - OH_3 \\ - OH_3 - OH_3 - OH_3 - OH_3 \\ - OH_3 - OH_3 - OH_3 - OH_3 \\ - OH_3 - OH_3 - OH_3 - OH_3 \\ - OH_3 - OH_3 - OH_3 - OH_3 \\ - OH_3 - OH_3 - OH_3 - OH_3 \\ - OH_3 \\ - OH_3 - OH_3 \\ - O$$

#### is called –

- (A) Williamson continuous etherification process(B) Etard reaction(C) Gatterman-Koch reaction
  - (D) Williamson Synthesis
- Q.21Reaction of phenol with chloroform in presence of dilute<br/>sodium hydroxide finally introduces which one of the<br/>following functional group ?[RE-AIPMT 2015]<br/> $(A)-CHCl_2$ <br/> $(C)-CH_2Cl$ (B)-CHO<br/>(D)-COOH
- Q.22 Which of the following reaction(s) can be used for the preparation of alkyl halides ? [RE-AIPMT 2015]
  - (I)  $CH_3CH_2OH + HCl \xrightarrow{Anhy. ZnCl_2}$
  - (II)  $CH_3CH_2OH + HCl \rightarrow$
  - $(III) (CH_3)_3 \tilde{COH} + HCl \rightarrow$

 $(IV) (CH_3)_2 CHOH + HCl \xrightarrow{Anhy. ZnCl_2}$ 

- (A) (IV) only (C) (I), (III) and (IV) only (D) (I) and (II) only
- Q.23 The reaction



#### [NEET 2016 PHASE 1]

[NEET 2018]

- (A) Williamson ether synthesis reaction
- (B) Alcohol formation reaction
- (C) Dehydration reaction

can be classified as

- (D) Williamson alcohol synthesis reaction
- Q.24 The heating of phenyl-methyl ethers with HI produces (A) iodobenzene (B) phenol [NEET 2017] (C) benzene (D) ethyl chlorides

(D) 
$$C_2H_5OH$$
,  $C_2H_5ONa$ ,  $C_2H_5Cl$   
**D 26** In the reaction:

$$\bigcirc^{\text{OH}} + \text{CHCl}_3 + \text{NaOH} \rightarrow \bigcirc^{\text{O}^-\text{Na}^+} \text{CHO}$$

The electrophile involved is  $_{\oplus}$ 

(A) Dichloromethyl anion  $(C HCl_2)$ 

(B) Formyl cation  $(\stackrel{\oplus}{C}HO)$ 

(C) Dichloromethyl cation  $(\overset{\oplus}{C}HCl_2)$ 

(D) Dichlorocarbene (: CCl<sub>2</sub>)

**QUESTION BANK** 











**Q.28** The compound that is most difficult to protonate is



# **ANSWER KEY**

	EXERCISE - 1																								
Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Α	А	А	А	D	В	В	А	С	D	С	В	А	В	С	С	А	А	В	А	С	В	С	В	С	С
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
Α	В	А	А	С	С	В	В	D	С	С	С	D	В	А	В	С	С	С	А	С	В	В	В	В	С
Q	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Α	В	D	D	С	В	С	С	А	С	А	В	А	В	С	D	А	А	А	А	А	D	D	С	D	D
Q	76	77	78	79	80	81	82	83	84	85	86	87	88	89											
Α	С	D	В	В	А	С	D	В	D	D	В	А	В	С											

#### **EXERCISE - 2** 16 19 22 25 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 17 18 20 21 23 24 Q С С В С С D С В D Α В D В А В А D D А D В В А В В D 33 38 Q 26 27 28 29 30 31 32 34 35 36 37 39 40 41 42 43 44 45 46 47 48 49 50 В С В В В С D С С D В В С С С Α В А D D D А А А А А Q 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 D С В С С С С С С С Α А А D А А А А В

EXERCISE - 3													
Q	1	2	3	4	5	6	7						
Α	2	1	2	3	2	1	9						

	EXERCISE - 4																								
Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Α	В	В	D	D	D	В	С	Α	D	A	D	С	Α	В	В	Α	D	D	А	В	D	Α	В	С	В
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39											
Α	Α	A	В	С	С	A	Α	D	В	С	A	С	В	В											

	EXERCISE - 5																								
Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Α	С	С	С	С	С	С	С	В	Α	В	А	А	С	С	D	В	D	В	С	D	В	С	А	В	D
Q	26	27	28																						
Α	D	В	D																						

#### 261



## **ALCOHOLS, PHENOLS AND**

# ETHERS

#### TRY IT YOURSELF-1

(1) (D). Due to less-effective hydrogen bonding solubility of  $Ph-CH_2-CH_2-OH$  becomes minimum

(2) (C). 
$$CH_3 - CH_2 \xrightarrow{H_2SO_4} CH_3 - CH_2 \xrightarrow{\oplus} H_{2O}$$

$$H_{2}^{\delta^{+}} \xrightarrow{\Theta} H_{2}^{\Theta} C = CH_{2}$$

$$H_{2}^{\Theta} C = CH_{2}$$

$$H_{2}^{\Theta} C = CH_{2}$$

(3) (C). 
$$CH_3 - C - OH \xrightarrow{\text{LiAlH}_4} CH_3 - CH_2$$

- (4) (A). As branching increases boiling point decreases.
- (5) (A). Compound which can form hydrogen bond with water are soluble and lower alcohols forming effective hydrogen bond with H<sub>2</sub>O. So, soluble in H<sub>2</sub>O.

(6) (D). 
$$\begin{array}{c} H & OH \\ | & | \\ -C - C - C \\ | & | \\ H & H \end{array} \xrightarrow{Conc. H_2SO_4} - C = C - | \\ -HOH \\ -HOH \end{array}$$

This reaction involve breaking of C - O' bond not O - H' bond.

(7) (B). 
$$CH_3 - C - OH + H_2O - C_2H_5 \xrightarrow{H^+/\Delta} Acetic acid$$

$$H \\ \parallel \\ CH_3 - C - OC_2H_5 + H_2O \\ Ethyl acetate$$

(8) (A).  $PCl_3$ ,  $PCl_5$ ,  $SOCl_2$ , HCl can replace – OH group but not  $Cl_2$ .

(9) (D). 
$$R - O - H + Na \rightarrow R - \overset{\Theta}{O} \overset{\oplus}{Na} + \frac{1}{2} H_2(\uparrow)$$

(10) (B).  $SO_2Cl_2$  cannot replace – OH group.

#### **TRY IT YOURSELF-2**



(2) (C). 
$$\bigcirc - O - CH_3$$
 Methoxybenzene (Anisol)  
(3) (B).  $\bigcirc OH$  (not Hydroxybenzene)  
Phenol

(4) (C). Electron in π bonds are π electrons & lone pair electrons which delocalises in the process of resonance are also counted as π electrons.

(6) (C). Acidic nature of o-nitrophenol is less than  $H_2CO_3$ . So, it does not react with Na<sub>2</sub>CO<sub>3</sub> solution.

(5)





(A). Electron withdrawing (-m/-R) nature of -NO<sub>2</sub> group increases acidic nature of p-nitrophenol.



(10) (C). Reimer-Tiemann reaction



262

**TRY SOLUTIONS** 



#### **TRY IT YOURSELF-3**



$$\begin{array}{c} C_{4}H_{10}O \\ Alcohol (4) \\ OH \\ (1) CH_{3} - CH_{2} - CH_{2} - CH_{2} \\ 1 - Butanol (1^{\circ}) \\ CH_{3} OH \\ (2) CH_{3} - CH - CH_{2} \\ 2 - methyl - 1 - propanol (1^{\circ}) \\ (3) CH_{3} - CH_{2} - CH - CH_{3} \\ 2 - propanol (2^{\circ}) \\ (4) CH_{3} - CH_{2} - CH_{3} \\ CH_{3} \end{array}$$

$$\begin{array}{c} CH_{3} OH \\ (2) CH_{3} - CH_{2} - CH_{2} \\ (2) CH_{3} - CH_{2} - O - CH_{3} \\ 2 - Methoxypropane \\ (3) CH_{3} - CH_{2} - O - CH_{2} - CH_{3} \\ Ethoxyethane \\ CH_{3} \end{array}$$

2-methyl-2-propanol (3°)

(2) (A). 
$$R - O - H + H - O - R \xrightarrow{H^+/\Delta}_{-HOH} \xrightarrow{R - O - R}_{Anhydride alcohol} \xrightarrow{(Ether)} (Ether)$$

(3) (C). Reaction of R - X with KCN does not produce ether.

(4) (A). Williamson's synthesis

$$CH_{3} \xrightarrow[]{(H_{3})}{CH_{3}} CH_{3} \xrightarrow[]{(H_{3})}{CH_{3}} CH_{3} \xrightarrow[]{(H_{3})}{CH_{3}} CH_{3} \xrightarrow[]{(H_{3})}{CH_{3}} CH_{3} \xrightarrow[]{(H_{3})}{CH_{3}} CH_{3} \xrightarrow[]{(H_{3})}{CH_{3}} CH_{3}$$

$$\begin{array}{c} CH_{3} & CH_{3} \\ CH_{3} - \overset{|}{\overset{C}{C}} - Br + \overset{\bigoplus}{\operatorname{Na}} \overset{\Theta}{\operatorname{OC}}_{2}H_{5} \rightarrow CH_{3} - \overset{|}{\overset{}{\overset{C}{C}}} + HOC_{2}H_{5} \\ \overset{|}{\underset{CH_{3}}{\overset{}{\operatorname{S}^{\circ}-alkyl halide}}} + HOC_{2}H_{5} \end{array}$$

(5) (B). Due to presence of line pair electron on O-atom. (6) (B).  $CH_3 - CH_2 - O - CH_2 - CH_3$ 

$$\xrightarrow{\text{Cl}_2} \text{CCl}_3 - \text{CCl}_2 - \text{O} - \text{CCl}_2 - \text{CCl}_3$$

(7) (D). 
$$C_2H_5OC_2H_5 \xrightarrow{Oxygen}$$
 Ether peroxide

(8) (C). 
$$R - \ddot{Q} - R \xrightarrow{H-I} R - I + HO - R$$

(9) (C). 
$$R - Br + NaOR' \longrightarrow R - O - R' + NaBr Unsymmetrical ether$$

(10) **(B).** 
$$CH_3 - CH_2 - O - CH_2 - CH_3$$

$$\xrightarrow[of Air]{O_2} H_3C-CH_2-O-CH-CH_3$$



### <u>CHAPTER-10:</u> <u>ALCOHOLS, PHENOLS AND ETHERS</u> <u>EXERCISE-1</u>

- (A). Methanol is also referred as wood alcohol or wood spirit or wood naphtha as the earliest method for its preparation was by destructive distillation of wood.
- (2) (A).  $CH_3OC_2H_5$  is known as ethyl methyl ether.

 (4) (D). Alcohols and phenols may be classified as mono, di, tri or polyhydric compounds depending on whether they contain one, two, three or many hydroxyl groups respectively in their structures.

$$C_{2}H_{5}OH \qquad \begin{array}{c} CH_{2}OH \\ CH_{2}OH \\ H \\ CH_{2}OH \end{array} \qquad \begin{array}{c} CH_{2}OH \\ H \\ CH_{2}OH \\ CH_{2}OH \end{array}$$



(5) (B). 
$${}^{5}CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH_{3}$$
  
 ${}^{1|}CH_{2}OH_{2}CH_{2}OH_{2}-ethylpentan-1-ol$ 

(6) (B). 1° alcohol is 
$$H - C - OH$$
  
H

(7) (A). Compounds containing (C<sub>sp<sup>3</sup></sub> – OH bond) In this class of alcohols the – OH group is attached to sp<sup>3</sup> hybridised carbon atom of an alkyl group. They are

hybridised carbon atom of an alkyl group. They a further classified follows :

- Primary, secondary and tertiary alcohols.
- Allylic alcohols.
- Benzylic alcohols.
- (8) (C). The IUPAC name of

is 5-chlorohexan-2-ol. Here, – OH is the principal functional group and – Cl is a substituent.

(9) (D). Compound : 
$$CH_3 - CH - CH_2CH_3$$
  
OH  
Common name : sec-butyl alcohol

IUPAC name : Butan-2-ol

Compound : 
$$CH_3 - CH - CH_2OH$$

Common name : isobutyl alcohol IUPAC name : 2-methylpropan-1-ol

Compound : 
$$CH_3 - CH_3 - OH_1 - OH_1 + OH_3 + CH_3$$

Common name : tert-butyl alcohol IUPAC name : 2-methylpropan-2-ol

$$\begin{array}{c} \text{Compound}: \text{CH}_2-\text{CH} -\text{CH}_2 \\ & \mid & \mid \\ & \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$$

Common name : Glycerol

IUPAC name : Propane-1, 2, 3-triol

- (10) (C). C-O-C angle in ether is about 110°.
- (B). In alcohols, the oxygen of the OH group is attached to carbon by a sigma (σ) bond formed by the overlap of sp<sup>3</sup> hybridised orbital of carbon with sp<sup>3</sup> hybridised orbital of oxygen.
- (12) (A). The C–O–H bond angle in alcohols is slightly less than the tetrahedral angles whereas the C–O–C bond angle in ether is slightly greater because of repulsion between the two bulky R groups.
- (13) (B). In ethers, the four electron pairs, i.e., the two bond pairs and two lone pairs of electrons on oxygen are arranged approximately in a tetrahedral arrangement.

(14) (C). 
$$CH_2 = CH_2 \xrightarrow{H_2SO_4} CH_3 - CH_2 - HSO_4$$

$$\xrightarrow{\text{Hydrolysis}} \text{CH}_3\text{CH}_2 - \text{OH} + \text{H}_2\text{SO}_4$$

(15) (C). 
$$C_2H_5 - NH_2 + HNO_2 \rightarrow C_2H_5OH + N_2 + H_2O_2$$

(16) (A).  $2(C_6H_{10}O_5)_n + nH_2O \xrightarrow[from germinated barley)]{Diastase} n(C_{12}H_{22}O_{11})$ Starch

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Maltase}} 2C_6H_{12}O_6$$
  
Glucose

$$C_6H_{12}O_6 \xrightarrow{Lymasc}{(from yeast)} 2C_2H_5OH + 2CO_2$$

17) (A). 
$$CO + H_2 \xrightarrow{CuO - ZnO - Cr_2O_3} CH_3OH$$
  
573K, 200 atm Methanol

$$\xrightarrow{H_2O} \xrightarrow{CH_3} \xrightarrow{C-OH} \text{ or } CH_3 \xrightarrow{I} \xrightarrow{C-OH} \xrightarrow{CH_3} \xrightarrow{I} \xrightarrow{C-OH} \xrightarrow{CH_3} \xrightarrow{I} \xrightarrow{CH_3} \xrightarrow{CH_3} \xrightarrow{I} \xrightarrow{CH_3} \xrightarrow{I} \xrightarrow{CH_3} \xrightarrow{CH_3} \xrightarrow{I} \xrightarrow{CH_3} \xrightarrow$$

(19) (A). Diborane  $(BH_3)_2$  reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.

264

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**Q.B. - SOLUTIONS** 



$$H_{3}C-CH = CH_{2} + (H-BH_{2})_{2}$$

$$\rightarrow H_{3}C-CH-CH_{2} - H_{3}C-CH=CH_{2}$$

$$H_{3}C-CH=CH_{2} - H_{3}C-CH=CH_{2}$$

$$(CH_{3}CH_{2}CH_{2})_{2}BH \xrightarrow{H_{3}C-CH=CH_{2}} (CH_{3}CH_{2}CH_{2})_{3}B$$
$$\xrightarrow{H_{2}O}{3H_{2}O_{2},OH^{-}} 3CH_{3}CH_{2}CH_{2}OH + B(OH)_{3}$$

The alcohol is formed by the addition of water to the alkene in a way opposite to the Markownikoff's rule. In this reaction, alcohol is obtained in excellent yield.

(20) (C). Alkenes react with water in the presence of acid as catalyst to form alcohols. In case of unsymmetrical alkenes, the addition reaction takes place in accordance Markownikoff's rule.

$$CH_3 - CH = CH_2 + H_2O \rightleftharpoons H^+ H_3C - CH - CH_3$$

(21) (B). Tertiary alcohols are formed by treating Grignard reagents either with ketones or excess of an ester other than formate which will give 2° alcohol.

(22) (C). 
$$CH_3COOC_2H_5 \xrightarrow{\text{LiAlH}_4/H_3O^+} \text{or } H_2/Pt \rightarrow$$
  
Ethyl acetate

(

$$CH_3CH_2OH + C_2H_5OH$$
  
The mechanism of the reaction

(23) (B). Mechanism : The mechanism of the reaction involves the following steps
 Step I : Protonation of alkape to form carbocation by

**Step I :** Protonation of alkene to form carbocation by electrophilic attack of  $H_3O^+$ .

 $H_2O + H^+ \rightarrow H_3O^+$ 

$$\sum C = C \left\langle +H - O - H \right\rangle = - \left\langle -C - C - C \right\rangle + H_{2}O$$

Step II : Nucleophilic attack of water on carbocation.

Step III : Deprotonation to form an alcohol.

(24) (C). Alcohols having less number of carbon atoms are more soluble in water.

(25) (C). 
$$CH_3 - CH_2 - OH \xrightarrow{Conc. H_2SO_4} CH_2 = CH_2 + H_2O$$

(26) (B). Lower alcohols are soluble in all solvents.

(27) (A). 
$$CH_3CH_2OH \xrightarrow{K_2Cr_2O_7} CH_3COOH$$

- (28) (A).  $CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O$ Esterification
- (29) (C). Alcohol is soluble in water due to H-bonding.

- (31) (B). KMnO<sub>4</sub> will oxidise initially formed aldehydes to carboxylic acids.
- (32) (B). The acidic character of alcohols is due to the polar nature of OH bond.

(33) (D). 
$$CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$$
  
Ethyl acetate

- (34) (C). Order of reactivity of different alcohols towards esterification is 1° alcohol > 2° alcohol > 3° alcohol due to increased steric hindrance in 2° and 3° alcohols.
- (35) (C). The tertiary carbocation formed during dehydration of 2-methyl-2-propanol is most stable.

$$\begin{array}{c} CH_{3} & CH_{3} & CH_{3} \\ CH_{3} - \overset{|}{\overset{C}{\underset{CH_{3}}{\overset{}}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{}}{\underset{CH_{3}}{\overset{C}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{H^{+}}{\underset{CH_{3}}{\overset{H^{+}}{\underset$$

(36) (C). More the number of methyl groups (electron releasing) lesser will be the acidity. Hence the reactivity towards sodium metal will be tertiary < secondary < primary</p>

(37) (D). 
$$\operatorname{RCH}_2\operatorname{OH} \xrightarrow{\operatorname{Oxidation}} \operatorname{RCHO}_{\operatorname{Aldehyde}} \xrightarrow{\operatorname{RCOOH}_{\operatorname{Carboxylic acid}}}$$

- (38) (B). The process of converting alkyl halides into alcohols involves substitution reaction.
- (39) (A). During the reaction carbocations are formed. 3° carbocation is more stable than 1°, hence the dehydration in 3° alcohol proceeds faster than 1° alcohol.

$$\begin{array}{c} CH_{3} & CH_{3} \\ CH_{3} - \overset{|}{\overset{C}{C}} - OH \xrightarrow{H^{+}} CH_{3} - \overset{|}{\overset{}{\overset{C}{C}}} - \overset{+}{OH_{2}} \\ CH_{3} & CH_{3} - \overset{|}{\overset{}{\overset{}{C}}} - \overset{+}{OH_{2}} \end{array}$$

$$\xrightarrow{-H_2O} CH_3 \xrightarrow{CH_3} CH_3 \xrightarrow{-H^+} CH_2 = \overset{CH_3}{\overset{|}{CH_3}}$$

(40) (B). Alcohols are soluble in Lucas reagent (conc. HCl and ZnCl<sub>2</sub>) while their halides are immiscible and produce turbidity in solution. In case of tertiary alcohols, turbidity is produced immediately as they form the halides easily. Primary alcohols do not produce turbidity at room temperature.



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(41) (C). 
$$C_2H_5OH \xrightarrow{\text{NaOH/I}_2} CHI_3$$
 (yellow ppt)  
Iodoform test

$$CH_3OH \xrightarrow{\text{NaOH/I}_2} \text{Noppt}$$

- (42) (C). Tertiary alcohol produces the turbidity immediately on the reaction with Lucas reagent.
- (43) (C).  $C_2H_5OH \xrightarrow{NaOH/I_2} CHI_3$   $CH_3COCH_3 \xrightarrow{NaOH/I_2} CHI_3$  $CH_3OH \xrightarrow{NaOH/I_2} No reaction$
- (44) (A). Ethyl alcohol gives positive iodoform test (i.e. yellow ppt. with I<sub>2</sub> and NaOH) CH<sub>3</sub>CH<sub>2</sub>OH + 4I<sub>2</sub> + 6NaOH →

$$CHI_3 + 5NaI + CH_3COONa + 3H_2O$$
  
ellow ppt

- (45) (C). The rate of reaction with Lucas reagent is 3°>2°>1°. Tertiary alcohols immediately react to give turbidity, secondary alchols after sometime and primary alcohols do not give turbidity until heated.
- (46) (B). The reaction of alcohol with lucas reagent is mostly an  $S_N^1$  reaction and the rate of reaction is directly proportional to the carbocation stability formed in the reaction, since  $3^\circ R OH$  forms  $3^\circ$  carbocation hence it will react fastest.
- (47) (B). 5-10 % methyl alcohol and remaining ethanol is called methylated spirit. It is also known as denatured alcohol because it is unfit for drinking.
- (48) (B). The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it colour) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol.
- (49) (B). Power alcohol 80% petrol and 20% ethyl alcohol
- (50) (C). Denaturing can also be done by adding 0.5% pyridine, petroleum naptha, CuSO<sub>4</sub> etc.



(52) (D).



- (53) (D). Chlorobenzene does not undergo hydrolysis on treatment with aqueous NaOH at 298K.
- (54) (C). Phenol has higher boiling point than toluene because of hydrogen bonding.

(55) (B). Of Benzene nucleus

(56) (C). 
$$\bigcirc^{OH} + CH_2N_2 \xrightarrow{HBF_4} \bigcirc^{O-CH_3}_{Anisole} + N_2$$

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(57) (C). –OH group in phenol can release electrons to the ring better than –CH<sub>3</sub> group in toluene. Cl atom has electron withdrawing effect which inhibits electrophile attack.



(58) (A). Kolbe's reaction : Phenoxide ion generated by treating phenol with NaOH is even more reactive than phenol towards electrophilic aromatic substitution.

Hence, it undergoes electrophilic substitution with  $CO_2$ , a weak electrophile ortho-hydroxybenzoic acid is formed as the main reaction product.







This reaction is Reimer-Tiemann reaction.

- (60) (A). Dehydration of IV is most facile since, it gives an aromatic compound.
  - Dehydration of III gives a conjugated diene which is stabilized by resonance.



Dehydration of II gives only cyclohexene which is not stabilized by resonance.



In contrast, phenol (I) does not undergo dehydration. Thus, the ease of dehydration is: IV > III > II > I.

- (61) (B). Phenol is less acidic than o-nitrophenol as electron withdrawing (- NO<sub>2</sub>) group increases the acidity of phenols while electron donating groups (-CH<sub>3</sub>, OCH<sub>3</sub>) decrease the acidity of phenols. Phenols are more acidic than alcohols.
- (62) (A). OH group in phenols is more strongly held compared to OH group in alcohols.
- (63) (B).



(64) (C).



(65) (D). Nitration of phenol with dilute nitric acid at low temperature (298 K), phenol yield a mixture of ortho and para nitrophenols.



(66) (A). o-Nitrophenol is stable due to intramolecular hydrogen bonding.

 $O \leftarrow N = O$ 

It is difficult to break the H-bonding when dissolved in water thus less soluble.

(67) (A). Phenol ( $C_6H_5OH$ ) will react with sodium hydroxide solution in water, as phenols are more acidic than alcohols.



- (69) (A). Phenol has higher boiling point than toluene because of hydrogen bonding.
- (70) (A). Phenol on reaction with excess of bromine water gives a white precipitate of 2, 4, 6-tribromophenol.



- (71) (D). Presence of electron withdrawing groups such as nitro group enhances the acidic strength of phenol and the presence of electron releasing groups such as alkyl group decreases the acidic strength of phenol.
- (72) (D). Compounds containing OH group directly attached to benzene ring are called phenolic compounds.



Benzenol o-Cresol Catechol

(73) (C). Phenol (all enols) can be oxidised by FeCl<sub>3</sub> to form coloured complexes. Alcohols, however, cannot get oxidised by FeCl<sub>3</sub>.

#### (74) (D).

**Q.B. - SOLUTIONS** 

- (a) Some phenols can be used as flavouring agents.
- (b) Some phenols can be used as perfumes.
- (c) Vanillin (present in oil of vanilla bean) is an example of phenol used as a flavouring agents.

(a) Phenol give deep blue or violet colour with neutral FeCl<sub>3</sub>.

$$3C_6H_5OH + FeCl_3 \rightarrow (C_6H_5O)_3Fe + 3HCl$$
  
Violet

(b) Phenol give liebermann's nitroso reaction.

Phenol in conc. 
$$H_2SO_4 \xrightarrow{NaNO_2} excess of water$$

Red colour  $\xrightarrow{\text{NaOH}}$  Blue colour

(c) Phenol produce a white precipitate of 2, 4,6- tribromophenol with bromine water.

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(76) (C). Williamson's synthesis

7) **(D).** 
$$CH_3OCH_3 \xrightarrow{Cl_2/NV} CH_3OCH_2Cl$$
  
Methoxymethane  
(Lowerether)  $\alpha$ -Chlorodimethylether

$$\xrightarrow{\text{CH}_3\text{MgBr}} \xrightarrow{\text{CH}_3\text{OCH}_2\text{CH}_3} \xrightarrow{\text{CH}_3\text{OCH}_2\text{CH}_3} \xrightarrow{\text{Methoxyethane}} (\text{Higher ether})$$

(78) (B).

(7'

$$CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{-C} O - CH_{3} + NaCl$$

$$CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3}$$

$$CH_{3} \xrightarrow{CH_{3}} Methyl-t butyl ether$$

(79) (B). Tertiary halide can involve elimination of HX to give alkene in presence of a base. Hence, a tertiary alkoxide and primary alkyl halide is taken for the reaction. CH<sub>3</sub>Br + NaOC(CH<sub>3</sub>)<sub>3</sub> [sod. t-butoxide]
 → CH<sub>3</sub>O-C(CH<sub>3</sub>)<sub>3</sub> + NaBr

methyl t-butyl ether

(80) (A). Williamson's synthesis : It is an method for the preparation of symmetrical and unsymmetrical ethers.  $RX + RO^{-}Na^{+} \rightarrow ROR + NaX$ 

(81) (C). 
$$CH_3CH_2OH \xrightarrow{H_2SO_4} C_2H_5OC_2H_5$$

267





- (82) (D).  $C_2H_5OH + CH_3CH_2CH_2OH \xrightarrow{Conc.H_2SO_4} C_2H_5OC_2H_5 + C_3H_7OC_3H_7 + C_2H_5OC_3H_7$
- (83) (B). Ether is basic because lone pairs of electrons are present on oxygen atom, R - Ö - R.
- (84) (D). Due to inter-molecular hydrogen bonding in alcohols boiling point of alcohols is much higher than ether.
- (85) (D).  $C_2H_5 O C_2H_5 + O_2 \xrightarrow{hv}_{25^{\circ}C} CH_3 CH(OOH) O C_2H_5$

- (87) (A). Ethers have lower boiling points than the corresponding isomeric alcohols because of absence of hydrogen bonding in ethers.
- (88) (B). The C O bonds in ethers are polar and thus, ethers have a net dipole moment.
- (89) (C). The large difference in the boiling point of alcohols and ethers is due to the presence of H bonding interaction in alcohols.

#### EXERCISE-2

 (C). Coconut oil + Alkali → Soap + Glycerol It is a saponification reaction.

(2) (C). 
$$C_6H_{12}O_6 \xrightarrow{Zymase} 2C_2H_5OH + 2CO_2$$
  
Glucose or Fructose Ethylalcohol

(3) (B). 
$$\bigcirc$$
 + CHCl<sub>3</sub> + 3NaOH  $\rightarrow$ 

Salicylaldehyde  $+ 3NaCl + 2H_2O$ 

(4) (D). Acetone reacts with Grignard's reagent to give tertiary alcohol.

$$(CH_3)_2C = O + CH_3MgBr \xrightarrow{H_2O} (CH_3)_3C - OH$$
  
ter-butyl alcohol  
(2-Methylpropan-2-ol)

(5) (B). 
$$C_2H_5MgBr + H_2C - CH_2 \xrightarrow{H_2O}$$

$$C_{2}H_{5}CH_{2}CH_{2}OH + MgBr(OH)$$
(A)
n-butylalcohol

(6) (B). Williamson's synthesis –

$$CH_3 - CH_2 - ONa + Cl - CH_2 - CH_3 \rightarrow$$

$$\mathrm{CH}_3 - \mathrm{CH}_2 - \mathrm{O} - \mathrm{CH}_2 - \mathrm{CH}_3$$

- (7) (A). Dehydration of alcohols gives ethers.
- (B). NaBH<sub>4</sub> and LiAlH<sub>4</sub> attacks only carbonyl group and reduce it into alcohol group. They do not attack on double bond.

$$C_6H_5 - CH = CHCHO \xrightarrow{\text{NaBH}_4} C_6H_5 - CH = CH.CH_2OH$$
  
cinnamic aldehyde

(9) (A). 
$$C_6H_6O^- + CH_3I \rightarrow C_6H_6OCH_3 + I^-$$

(10) (C). 
$$CH_3OH + Na \rightarrow CH_3ONa + \frac{1}{2}H_2$$
  
 $1 \text{ mole } 1 \text{ mole } 1/2 \text{ mole } 1/2 \text{ mole}$ 

(11) (D). 
$$3CH_3CH_2CH_2CH_2 - OH + PBr_3 \rightarrow$$

$$3CH_3CH_2CH_2CH_2 - Br + H_3PO_3$$

(12) (D). 
$$CH_3 - CH - CH_3 \xrightarrow{[O]} CH_3 - C - CH_3$$
  
 $\downarrow \\ OH O$ 

(13) (C). 
$$CH_3 - CH - CH_2 - CH_3 \xrightarrow{[0]} CH_3 - C - CH_2CH_3$$
  
OH

(15) (D). 
$$CH_2 - CH - CH_2$$
  
| | |  
OH OH OH

Glycerol is trihydric alcohol.

(16) (B). 
$$CH_2 - OH$$
  
 $CH - OH$   
 $H$   
 $CH_2 - OH$ 

One secondary and two primary alcoholic groups.

(17) (D). RMgBr 
$$+ O_2 \rightarrow R - OMgBr$$
  
Grignard reagent

$$\xrightarrow{\text{hydrolysis}} R - OH + Mg \langle OH \rangle$$

(18) (C). 
$$CH_3 - OH + CH_3 Mg - X \rightarrow CH_4 + CH_3 O - Mg - X$$

**19)** (**B**). 
$$\begin{array}{c} CH_2 - OH & CH_2 - I & CH_2 \\ | \\ CH - OH & \xrightarrow{P_4 + I_2} & | \\ | \\ CH_2 OH & CH_2 - I & CH_2 - I \\ Unstable & Allyl iodide \end{array}$$

20) (B). 
$$C_2H_5OH + R - Mg - X \rightarrow \underset{Alkane}{RH} + C_2H_5OMgX$$
  
 $C_3H_7OH + R - Mg - X \rightarrow RH + C_3H_7OMgX$ 

(21) (A). 
$$C_2H_5OH \xrightarrow{Pt} CH_3CHO$$

(22) (D). Traces of water from ethanol is removed by reacting with Mg metal.

(23) (B). 
$$CH_3CH_2 - OH + HO - CH_2 - CH_3$$

$$\xrightarrow{\text{Conc. } H_2\text{SO}_4} \text{CH}_3\text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_3 + \text{H}_2\text{O}}_{\text{Diethyl ether}}$$

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(24) (B). Hydrogen bonding :

- (25) (D). Tertiary alcohols react fastest with hydrogen halides.2 methyl propan-2-ol is a tertiary alcohol.
- (26) (B). Aspirin or Acetyl salicylic acid.
- (27) (B). CH<sub>3</sub>OH has highest boiling point because of hydrogen bonding.

(28) (B). 
$$CH_3OH + \frac{1}{2}O_2 \xrightarrow{Cu} HCHO + H_2O$$

(29) (A).

(30) (D). 
$$C_2H_5OC_2H_5 \xrightarrow{\text{Red P/HI}}_{\text{Cleavage of ethers}} 2C_2H_5I \xrightarrow{\text{Red P/HI}}_{\text{Reduction}} 2C_2H_6 \xrightarrow{\text{Ethane}}_{\text{Ethane}} 2C_2H_6$$
  
(30) (D).  $C_2H_5OC_2H_5 + O_2 \rightarrow CH_3 - CH - O - C_2H_5 \xrightarrow{|}_{O - OH}_{\text{Ether peroxide}}$ 

- (31) (B). Methanol has high boiling point than methyl thiol because there is intermolecular hydrogen bonding in methanol and no hydrogen bonding in methyl thiol.
- (32) (C).  $CH_2OH$  anh.  $ZnCl_2$   $CH_3CHO$  $H_2OH$   $-H_2O$  Acetaldehyde
- (33) (D). Ethyl alcohol give positive iodoform test (i.e. yellow ppt. with I<sub>2</sub> and NaOH)

 $CH_3CH_2OH + 4I_2 + 6NaOH \rightarrow$ 

$$CHI_3 + 5NaI + CH_3COONa + 3H_2O$$
  
yellow ppt.

(34) (D). 
$$C_2H_5OH \xrightarrow{Conc H_2SO_4} C_2H_4 + H_2O$$
  
170°C

- (35) (D). Pyridinium chlorochromate oxidises an alcoholic group selectively in the presence of carbon-carbon double bond.
- (36) (C). Primary alcohols readily form ether when heated with conc.  $H_2SO_4$ .

(37) (A). 
$$(H_{CH_3}) \xrightarrow{H^+} (H_{\Delta}) \xrightarrow{CH_3} (H_{1-Methylcyclohexanol}) \xrightarrow{H^+} (H_{\Delta}) \xrightarrow{CH_3} (H_{1-Methylcyclohexene}) \xrightarrow{H^+} (H_3CH_2CH_2OH) \xrightarrow{H^+} (H_3CH_2CH_2CH_2OH) \xrightarrow{H^+} (H_3CH_2CH_2CH_2OH) \xrightarrow{H^+} (H_3CH_2CH_2OH) \xrightarrow{H^+} (H_3CH_2CH_2OH) \xrightarrow{H^+} (H_3CH_2OH) \xrightarrow{H^+} (H_3CH_2CH_2OH) \xrightarrow{H^+} (H_3CH_2OH) \xrightarrow{H^+} (H_3CH_2OH) \xrightarrow{H^+} (H_3OH) \xrightarrow$$

ODM ADVANCED LEARNING

- (39) (D). Methanol is a colourless liquid and boils at 337 K. It is highly poisonous in nature. Ingestion of even small quantities of methanol can cause blindness and large quantities causes even death. It is used as solvent in paints, varnishes and chiefly for making formaldehyde.
- (40) (B). Presence of electron releasing group decreases the acidity of the alcohols. Hence t < s < p.  $CH_3OH > C_2H_5OH > (CH_3)_2CHOH > (CH_3)_3COH$ .

- (42) (B). 2,4,6- Trinitrophenol is commonly known as picric acid.
- (43) (A).  $C_4H_{10}O$  can have two structures:  $CH_3CH_2CH_2CH_2OH$  and  $C_2H_5OC_2H_5$ . Since it does not react with Na metal, it can not be an alcohol.  $C_2H_5OC_2H_5$  + HI (excess)  $\rightarrow 2C_2H_5I$  + H<sub>2</sub>O
- (44) (C). Electron releasing inductive effect of -OCH<sub>3</sub> group facilitates the protonation of alcohol involved in dehydration mechanism.
- (45) (B). Aspirin possesses analgesic, antiinflammatory and antipyretic properties.

Acetylation of salicylic acid produces aspirin.

$$\bigcup_{\text{Salicylic acid}}^{\text{OH}} + (\text{CH}_3\text{CO})_2\text{O} \xrightarrow{\text{H}^+} \xrightarrow{\text{OCOCH}_3}_{\text{Acetylsalicylic acid (Aspirin)}}$$

+CH<sub>3</sub>COOH

(46) (C).

**Q.B. - SOLUTIONS** 



- (47) (A). Presence of two electron withdrawing  $-NO_2$  groups in the ring makes 2, 4-dinitrophenol a stronger acid than phenol. Hence it reacts with aqueous  $Na_2CO_3$ solution to form sodium salt thus making it soluble in  $Na_2CO_3$ .
- (48) (C). 2-Chloroethanol is more acidic due to -I effect of chlorine.

(49) (C). 
$$C_2H_5OH(X) + HI \rightarrow C_2H_5I + H_2O$$
  
 $CH_3OCH_3(Y) + HI \rightarrow CH_3I + CH_3OH$ 

(50) (A). R-CH<sub>2</sub>OH+2 (O) → RCOOH+H<sub>2</sub>O When primary alcohol is oxidized, two hydrogens are removed and one oxygen is added to the molecule. Hence, molecular mass increases by 14 units.



(51) (D). 2-methyl propan-2-ol is an example for tertiary alcohol. Tertiary alcohol gives turbidity immediately with lucas reagent.





(53) (B). Power of alcohol is mixture of absolute alcohol and petrol.

(54) (C). 
$$\bigcirc$$
 + CH<sub>3</sub> - CH - CH<sub>3</sub>  $\xrightarrow{\text{Anhy. AlCl}_3}_{\text{Cl}}$ 



$$\xrightarrow{\text{dil.} \text{H}_2\text{SO}_4}_{100^\circ\text{C}} \rightarrow \text{Phenol} + \text{CH}_3\text{COCH}_3$$

(55) (C). 
$$CH_3MgI + ROH \rightarrow CH_4 + Mg < 0.44g$$
  
? 22400 cm<sup>3</sup>

$$\therefore \text{ Molecular mass of alcohol} = \frac{0.44 \times 224000}{112} = 88$$

If the alcohol with PCC gives a carbonyl compound, the alcohol must be  $2^{\circ}$  alcohol. Hence, answer is either (A) or (C). But as the molecular mass is 88, the answer is (C).

(56) (A). 
$$H + CH_3MgBr \xrightarrow{ether}$$

$$\begin{array}{c} CH_3 \text{ O}-MgBr \\ H_3C - \overset{|}{C} - \overset{|}{C} - H \\ H \\ H \\ H \\ CH_3 \end{array} \xrightarrow{H_2O/H^+} H_3C - \overset{CH_3 OH}{H} \\ H_3C - \overset{|}{C} - H \\ H \\ H \\ H \\ CH_3 \end{array}$$

$$\begin{array}{c} CH_3 & OH \\ | & | \\ H_3C - CH - CH - CH_3 \\ 4 & 3 & 2 & 1 \end{array}$$
 (3-methylbutan-2-ol)



(58) (D). Due to less-effective hydrogen bonding solubility of 
$$Ph - CH_2 - CH_2 - OH$$
 becomes minimum

(59) (C). 
$$CH_3 - CH_2 \xrightarrow{H_2SO_4}{-HSO_4} CH_3 - CH_2 \xrightarrow{\Theta}{-H_2O}$$

$$H_{1}^{\delta +} \xrightarrow{\Theta}_{H_{2}C - CH_{2}} \xrightarrow{H_{2}C} H_{2}C = CH_{2}$$

(60) (C). 
$$CH_3 - C - OH \xrightarrow{\text{LiAlH}_4} CH_3 - CH_2$$

- (61) (A). As branching increases boiling point decreases.
- (62) (A). Compound which can form hydrogen bond with water are soluble and lower alcohols forming effective hydrogen bond with H<sub>2</sub>O. So, soluble in H<sub>2</sub>O.

(63) (A). 
$$\bigcirc^{\text{Cl}} \xrightarrow{\text{NaOH/CuCl}_2} \xrightarrow{\text{OH}} (\text{Dow's process})$$

(64) (C). 
$$\bigcirc$$
  $O - CH_3$  Methoxybenzene (Anisol)

- (65) (C). Catechol
- (66) (C). Electron in  $\pi$  bonds are  $\pi$  electrons & lone pair electrons which delocalises in the process of resonance are also counted as  $\pi$  electrons.

(67) (A). 
$$R - O - H + H - O - R \xrightarrow{H^+/\Delta} R - O - R$$
  
Alcohol Alcohol (Ether)

(68) (B). Due to presence of lone pair electron on O-atom.

#### **EXERCISE-3**

- (1)
- **(2)** 1
- (3) 2

2

- (4) **3.** Primary alcohols : (i), (ii) & (iii)
- (5) 2. Secondary alcohols : (iv) & (v)
- (6) 1. Tertiary alcohols: (vi)
  (7) 9. X=8, Y=5, Z=4

C-CH<sub>3</sub>

**(B).** O – H---O – H---O – H

Ŕ **(D).**  $CH_2 = CH - CH_2OH$  **Q.B. - SOLUTIONS** 



#### **EXERCISE-4**

| R

(C). Sequence of dehydration of alcohol

 $+ CHCl_3 + NaOH$ 

OH

 $3^{\circ} > 2^{\circ} > 1^{\circ}$ 

(**D**). The general formula  $C_n H_{2n} O_2$  represents carboxylic

CH<sub>3</sub>

OH

CH<sub>3</sub>

СНО

CH(OH)-COOH

(13) (A).



This is Kolbe's synthesis.

- (B). 3° alcohols react fastest with ZnCl<sub>2</sub>/conc. HCl due (15)to formation of 3° carbocation and
  - 2-methyl propan-2-ol is the only 3° alcohol ....





HCN

(1)

(2)

(3)

(4)

(5)

(6)

(7)

(8)

**(B)**.

Ŕ

acids.

(D) Butane-2-one

(B). Benzaldehyde

CH<sub>3</sub>

ЬH

CH<sub>3</sub>

(10)(A). Mechanism :  $CHCl_3 + OH^- \longrightarrow Cl_3C^- + H_2O \longrightarrow Cl^- + : CCl_2$ Dichloromethilene (electrophile)



H<sup>+</sup>/HOH

(12) (C). 
$$CH_3CH_2OH \xrightarrow{P+I_2} CH_3 - CH_2 - I$$
  
[A]



Trans isomers is more stable & main product here

$$C = C + CH(CH_3)_2$$
  
(trans isomer)

(17) **(D).** KBr (aq.) + KBrO<sub>3</sub> (aq.) 
$$\rightarrow$$
 Br<sub>2</sub> (aq.)

$$\bigcup_{i=1}^{OH} + \operatorname{Br}_{2}(\operatorname{aq}) \longrightarrow \bigcup_{i=1}^{Br} \bigoplus_{\substack{Br\\2,4,6-\text{tribromophenol}}}^{OH} \operatorname{Br}_{2,4,6-\text{tribromophenol}}$$

- (18) (D). Neutral  $FeCl_3$  reacts with phenol and give violet coloured complex.
- (19) (A). The Cannizzaro product of given reaction yields 2, 2, 2-trichloroethanol.



OII



(21) (D).  $CH_3 - CH - CH_2 - OH$ 

ĊН3

isobutyl alcohol does'nt give positive iodoform test.

(22) (A). 
$$HO$$

Wolf-Kishner reduction  $CH = CHCH_2CH_3$ HO

 $\rm NH_2NH_2/OH^-$ 

- OH group and alkene are acid-sensitive groups so clemmensen reduction can not be used.

(23 (B). The reaction of alcohol with lucas reagent is mostly an  $S_N^1$  reaction and the rate of reaction is directly proportional to the carbocation stability formed in the reaction, since  $3^\circ R - OH$  forms  $3^\circ$  carbocation hence it will react fastest.



- (Aspirin) (25) (B). PCC is mild oxidising agent, it will convert
  - $RCH_2OH \xrightarrow{PCC} RCHO$















(30) (C). Cummene hydroperoxide reaction





- \* Oleic acid is also soluble in NaHCO<sub>3</sub>.
- \* o-toluidine is not soluble in NaOH as well as NaHCO<sub>3</sub>.

\* Benzamide is also not soluble in NaOH & NaHCO<sub>3</sub>.(32) (A).







Q.B. - SOLUTIONS







- (36) (A). When negative charge is delocalised with electron withdrawing group like (NO<sub>2</sub>) then stability increases.
  - a. Negative charge is delocalised with  $NO_2$  group.
  - b. Negative charge is delocalised with carbon of alkene.
  - c. Negative charge is localised.



There is not any resonance in  $CH_3$ –OH. Resonance is poor in p-Ethoxyphenol than phenol.

(39) (B). In A, extensive inter-molecular H-bonding is possible while in B there is no Inter-molecular H-bonding.

#### EXERCISE-5

(1) (C). Phenols are more acidic than alcohol as they are resonance stabilised whereas alcohols are not. Further nitro group is an electron withdrawing group hence helps in stabilizing the negative charge on oxygen hence equilibrium shifts towards fowards direction and hence  $H^+$  remove easily, wheres –  $CH_3$  is an electron donating group hence density increases on the oxygen and helps in destabilizing the product hence the equilibrium shifts in backward direction, thus removal of  $H^+$  becomes very difficult.

- (2) (C). Alkanols :  $C_n H_{2n+2}O$  [ $C_n H_{2n+1}OH$ ]
- (3) (C). Ethylene oxide when treated with Grignard reagent gives primary alcohol.

$$\begin{array}{c} CH_2 \\ CH_2 \\ CH_2 \end{array} \rightarrow HRMgX \rightarrow H_2O \\ H R - CH_2 - CH_2 - OH + Mg \\ \end{array}$$

(4) (C). In case of unsymmetrical ethers, the site of cleavage depends on the nature of alkyl group e.g.,  $CH_3 - O - CH (CH_3)_2 + HI$ 

$$\xrightarrow{373K} CH_3I + (CH_3)_2 CHOH$$
Methyl Isopropyl  
iodide alcohol

The alkyl halide is always formed from the smaller alkyl group.

(5) (C). In the cleavage of mixed ethers with two different alkyl groups, the alcohol and alkyl iodide that form depend on the nature of alkyl group. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide therefore

$$CH_3 - CH - CH_2 - O - CH_2 - CH_3 + HI$$

$$|$$

$$CH_3$$

$$\xrightarrow{\text{CH}_3} \overset{\text{CH}_3}{\longrightarrow} \text{CH}_3 - \overset{|}{\text{CH}} - \text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{II}$$

6) (C). 
$$CH_3CH_2OH \xrightarrow{PBr_3} CH_3CH_2Br$$

$$\xrightarrow{\text{Alc. KOH}} \text{CH}_2 = \text{CH}_2 \xrightarrow{(i) \text{H}_2\text{SO}_4} \text{CH}_3\text{CH}_2 - \text{HSO}_4$$
$$\xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{OH}$$

7) (C). 
$$\xrightarrow{\text{CH}_2\text{OH}}_{\text{CH}_2\text{OH}} \xrightarrow{\text{HIO}_4}_{\text{CH}_2\text{O} + \text{CH}_2\text{O}}$$

(

(

(9)



(A). Higher the tendency to give a proton, higher is the acidic character, and tendency to lose a proton depends upon the stability of intermediate, i.e., carbanion formed.

2, 4, 6-trinitrophenol after the loss of a proton gives 2,4,6-trinitrophenoxide ion which is stabilised by resonance, -I effect and -M effect, thus is most acidic among the given compounds.

Phenol after losing a proton form phenoxide ion which is also stabilised by resonance, -M and -I effects but is less stabilised as compared to 2, 4, 6-trinitrophenoxide ions.

Thus, it is less acidic as compared to 2,4,6-trinitrophenol. (CH<sub>3</sub>COOH) after losing a proton

gives acetate  $(CH_3C \swarrow_0^{-})$  ion which is stabilised by

only resonance. However, it is more resonance stabilised as compared to a phenoxide ion, thus more acidic as compared to phenol. 2,4,6-trinitrophenol, however, is more acidic than acetic acid due to the presence of three electron withdrawing  $-NO_2$  groups. Cyclohexanol gives an anion that is least stable among the given, thus, it is least acidic. Hence, the correct order of acidic strength is 2, 4, 6-trinitrophenol > acetic acid > phenol > cyclohexanol.

- (10) (B). Presence of electron withdrawing substituent increases the acidity while electron relasing substituent, when present, decreases the acidity. Phenyl is an electron withdrawing substituent while  $-CH_3$  is an electron releasing substituent. Moreover, phenoxide ion is more resonance stabilised as compared to benzyloxide ion, thus releases proton more easily. That's why it is a strong acid among the given.
- (11) (A). In phenols, the presence of electron releasing groups decreases the acidity, whereas presence of electron withdrawing groups increase the acidity, compared to phenol. Among the meta and para-nitrophenols, the latter is more acidic as the present of  $-NO_2$  group at para position stabilises the phenoxide ion to a greater extent than when it is present at meta position. Thus, correct order of acidity is :

(12) (A). 
$$\begin{array}{c} CH_2OH & CH_2I \\ | & \\ CHOH + 3HI \xrightarrow{\text{Warm}} & CHI \\ | & \\ CH_2OH & CH_2I \\ Glycerol & 1, 2, 3-triiodopropane \\ (unstable) \end{array}$$

$$\xrightarrow[-I_2]{\begin{array}{c} CH_2 \\ || \\ CHI \\ | \\ CH_2I \\ Allyl iodide \end{array}} \xrightarrow[HI(excess)]{\begin{array}{c} CH_3 \\ | \\ CH_1 \\ CH_2I \\ (unstable) \end{array}}$$



(13) (C). Compounds having either group or  $CH_3CHOH$ group, give iodoform when warmed with  $I_2$  and NaOH.

Thus, 
$$CH_3 - CHOH$$
,  $CH_3 - \overset{O}{C} - CH_3$ ,  $CH_3 - CHOH$ 

give iodoform when warmed with  $I_2$  and NaOH, (Remember, NaOI oxidises  $CH_3CH_2OH$  to  $CH_3CHO$ , thus it gives positive iodoform test.)

(14) (C). 
$$CH_{3} - \overset{H_{3}}{CH} - \overset{H_{3}}{CH} - \overset{H_{4}}{CH} - CH_{3} - \overset{H_{4}^{+}/heat}{OH}$$
  

$$CH_{3} - \overset{CH_{3}}{CH} - \overset{H_{4}}{CH} - CH_{3} - \overset{H_{4}^{+}/heat}{CH} \rightarrow \overset{H_{3}^{-}/heat}{CH} \rightarrow \overset{H_{3}^{-}/heat}{CH} \rightarrow \overset{CH_{3}}{CH} - \overset{H_{4}^{-}}{CH} - \overset{H_{4}^{-}}{CH} \rightarrow \overset{H_{4}^{+}}{CH} \rightarrow \overset{CH_{3}}{-H^{+}} \rightarrow \overset{CH_{3}}{H} - \overset{CH_{3}}{CH} \rightarrow \overset{CH_{3}}{H} - \overset{CH_{3}}{H} - \overset{CH_{3}}{H} \rightarrow \overset{CH_{3}$$

(15) (D). 
$$CH_3 - Br \xrightarrow{KCN} CH_3 - CN \xrightarrow{H_3O^+} CH_3 - CN \xrightarrow{H_3O^$$

$$\begin{array}{c} \text{CH}_3 - \text{COOH} \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_2 - \text{OH} \\ \text{(B)} & \text{(C)} \\ \text{Ethylalcohol} \end{array}$$

(16) (B). Glycol is used as an antifreeze in automobiles.

(17) (D). C – O bond cleavage of ether depends on mechanism involved in reaction which can be  $S_N 1$  or  $S_N 2$ . If any one group can form stable carbocation like tertiary butyl group then reaction follows  $S_N 1$  mechanism

$$\begin{array}{c} CH_{3} \\ H_{3} \xrightarrow{I}{C} - O - CH_{3} \xrightarrow{Hot \& conc. HI} & CH_{3} \xrightarrow{I}{C} O - CH_{3} \\ H_{3} \xrightarrow{I}{C} H_{3} \xrightarrow{I} O - CH_{3} \\ CH_{3} \xrightarrow{I} O - CH_{3} \\ H \end{array}$$

$$\xrightarrow{\text{CH}_{3}} \xrightarrow{\text{CH}_{3} - \overset{\square}{C} \oplus + \text{CH}_{3} - \text{OH}}_{\substack{I \oplus \\ \downarrow \\ \text{CH}_{3} \text{ alcohol}}} \xrightarrow{\text{I}^{\Theta}} \xrightarrow{\text{CH}_{3} - \overset{\square}{C} - \text{I}}_{\substack{I \oplus \\ \downarrow \\ \text{CH}_{3}}}$$

274

**Q.B. - SOLUTIONS** 

(26)





- (19) (C). o-nitrophenol is weaker acid than  $HCO_3^{-1}$ .
- (20) (D). It is Williamson-synthesis reaction.
- (21) (B). Reimer Tieman reaction

$$\overset{OH}{\longmapsto} + CHCl_3 + NaOH \rightarrow \overset{OH}{\bigcup} \overset{CHO}{\longleftarrow}$$

- (22) (C). (I) and (IV) can be used due to presence of anhydrous ZnCl<sub>2</sub> (III) gives alkyl halide due to formation of more stable carbocation.
- (23) (A). Williamson ether synthesis reaction involves the treatment of sodium alkoxide with a suitable alkyl halide to form an ether.
- (24) (B).

$$\begin{array}{c} \text{Ph-}\ddot{\text{O}}\text{-}\text{CH}_{3} \xrightarrow{\text{H}^{+}} \text{Ph-}\overset{\text{Ph-}}{\text{O}}\text{-}\text{CH}_{3} \xrightarrow{\text{I}^{\Theta}} \text{Ph-}\text{OH+}\text{I-}\text{CH}_{3} \\ \downarrow \\ \text{H} \end{array} \xrightarrow{\text{Ph-}} \text{Ph-}\text{OH+}\text{I-}\text{CH}_{3} \xrightarrow{\text{I}^{\Theta}} \text{Ph-}\text{OH+}\text{I-}\text{CH}_{3} \end{array}$$

(25) (D).  $C_2H_5OH \xrightarrow{Na} C_2H_5O^-Na^+$ (A) (B)  $\downarrow PCl_5$   $C_2H_5Cl$ (C)  $C_2H_5O^-Na^+ + C_2H_5Cl \xrightarrow{S_N2} C_2H_5OC_2H_5$ 

(B) (C)

So the correct option is (D).

**(D).** It is Reimer-Tiemann reaction.

The electrophile formed is :CCl<sub>2</sub> (Dichlorocarbene) according to the following reaction

$$\mathrm{CHCl}_3 + \mathrm{OH}^- \Longrightarrow \overset{\Theta}{\mathrm{C}} \mathrm{Cl}_3 + \mathrm{H}_2 \mathrm{O}$$

$$\overset{(0)}{C}Cl_3 \rightarrow :CCl_2 + Cl^{-1}$$

Electrophile



(28) (D). Due to involvement of lone pair of electrons in resonance in phenol, it will have positive charge (partial), hence incoming proton will not be able to attack easily.