

Chapter 26 Alcohol, Phenol and Ether

Hydroxy compounds

Hydroxy compounds are those compounds in which the hydroxy group, - OH is directly linked with the aliphatic or aromatic carbon.

Monohydric alcohols

These are compound containing one hydroxyl group. Their general formula is $C_n H_{2n+2}O$

(1) Preparation : (i) From alkyl halide

 $\begin{array}{l} C_2H_5Br + KOH \rightarrow C_2H_5OH + KBr \\ \text{Bromoethane} & (Aqueous) \rightarrow C_2H_5OH + KBr \\ C_2H_5Br & + AgOH \\ \text{Bromoethane} & \rightarrow C_2H_5OH + AgBr \\ \text{Bromoethane} & \text{Ethanol} \end{array}$

□ 1° alkyl halide gives good yield of alcohols.

 $\hfill\square$ 2° alkyl halide gives mixture of alcohol and alkene.

 \Box 3° alkyl halide gives alkenes due to dehydrohalogenation.

(ii) From alkenes : (a) Hydration

Indirect process :

$$CH_{2} = CH_{2} + HOSO_{2}OH \rightarrow CH_{3}CH_{2}OSO_{2}OH$$

Ethene Sulphuric acid Ethylhydrogen sulphate

$$\xrightarrow{H_{2}O} CH_{3}CH_{2}OH + H_{2}SO_{4}$$
Ethanol

In case of unsymmetrical alkenes

Propene $CH_3 - CH - CH_3 \xrightarrow{H_2O} CH_3 - CH - CH_3$ $OSO_2OH \xrightarrow{OH} OH$ $CH_3 \xrightarrow{CH_3} CH_3$

 $CH_3CH = CH_2 + HOSO_2OH \xrightarrow{\text{Markowniko ff's}}$



(b) Oxymercuration-demercuration

>C = C

$$\begin{pmatrix} +H_2O + Hg(OAc)_2 & \xrightarrow{Oxy \text{ mercuration}} \\ & \xrightarrow{\text{Mercuricacetate}} \\ & -\overset{|}{C}-\overset{|}{C}-\overset{NaBH_4}{\xrightarrow{\text{Demercuration}}} - \overset{C}{C}-\overset{C}{C}- \overset{-}{C} \\ & \stackrel{|}{OH} HgOAc & \xrightarrow{OHH} H \\ & \xrightarrow{\text{Alcohol}} \end{pmatrix}$$

Alcohol

This reaction is very fast and produces the alcohol in high yield. The alcohol obtained corresponds to Markownikoff's addition of water to alkene.

(c) *Hydroboration oxidation* (HBO) : (Antimarkownikoff's orientation)

$$C = C \left\langle +H - BH_2 \rightarrow - \begin{array}{c} & | & | & | & | & | & | \\ C - C - C - C - C - C - C - H_2 O_2, OH^- \rightarrow & - \begin{array}{c} & | & | & | & | & | \\ C - C - C - C - H_1 & | & | & | & | \\ H - BH_2 & H - OH_1 & | & | & | & | \\ H - BH_2 & H - OH_1 & | & | & | \\ H - BH_2 & H - OH_1 & | & | & | \\ H - BH_2 & H - BH_2 & | & | & | \\ H - BH_2 & H - BH_2 & | & | & | \\ H - BH_2 & H - BH_2 & | & | & | \\ H - BH_2 & H - BH_2 & | & | & | \\ H - BH_2 & H - BH_2 & | & | \\ H - BH_2 & H - BH_2 & | & | \\ H - BH_2 & H - BH_2 & | & | \\ H - BH_2 & H - BH_2 & | & | \\ H - BH_2 & |$$

Diborane is an electron defficient molecule. It acts as an electrophile reacting with alkenes to form alkyl boranes R_3B .

$$R - CH = CH_2 + H - BH_2 \rightarrow R - CH - CH_2 \xrightarrow[]{RCH = CH_2} H_B BH_2$$

$$H_B BH_2$$
Alkyl borane
$$(D, CH, CH) = DH = \frac{RCH = CH_2}{RCH = CH_2} + (DCH, CH) = D$$

$$(R CH_2 CH_2)_2 BH \xrightarrow{RCH_2CH_2} (R CH_2 CH_2)_3 B$$

Dialkyl borane Trialkyl borane

□ Carbocation are not the intermediate in HBO hence no rearrangement take place.

(iii) By reduction of carbonyl compounds

$$RCHO + H_{2} \xrightarrow{Pd} RCH_{2}OH$$
Aldehyde
$$RCOR' + H_{2} \xrightarrow{NaBH_{4}} R - CH - R'$$
Ketone
$$RCOR' + H_{2} \xrightarrow{NaBH_{4}} R - CH - R'$$
OH
Secondary alcohol
$$CH_{2} = CH_{2} \xrightarrow{H_{3}O^{+}} CH_{3} \xrightarrow{\oplus} CH_{3} \xrightarrow{H_{2}O} CH_{3}$$

$$H_{3}O^{+} CH_{3} \xrightarrow{\oplus} CH_{3} \xrightarrow{H_{3}O} CH_{3}$$

 $LiAlH_4$ also reduces epoxides into alcohol :

$$CH_2 - CH_2 + LiAlH_4 \rightarrow CH_3 - CH_2OH$$

Hydride selectively attacks the less alkylated carbon of the epoxide.

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

(iv) By reduction of carboxylic acids and their derivatives

$$\begin{array}{c} R - COOH & \xrightarrow{(i) LiAlH_4} & RCH_2OH \\ Carboxy lic acid & \xrightarrow{(ii) H_2O} & primary alcohol \\ \hline RCOOH \\ Carboxy lic acid & \xrightarrow{RCOOR} R' \xrightarrow{H_2} RCH_2OH + R'OH \\ \hline Cataly st \end{array}$$

Esters are also reduced to alcohols

(Bouveault Blanc reaction)

$$\begin{array}{c} O \\ \parallel \\ CH_3 - C - OCH_3 + 4[H] \xrightarrow{Na/C_2H_5OH} CH_3CH_2OH + CH_3OH \\ Methylacetate \\ (Ester) \\ Ethanol \\ \end{array} \xrightarrow{Na/C_2H_5OH} CH_3CH_2OH + CH_3OH \\ Hethanol \\ Hethanol \\ \end{array}$$

□ Reduction with aluminium isopropoxide is known as Meerwein-Ponndorff verley reduction (MPV) reduction.

$$Me_{2}C = O + (CH_{3})_{2}CHOH \xrightarrow{Al(OCHMe_{2})}$$
Isopropy lalcohol
$$Me_{2}CHOH + \frac{CH_{3}}{CH_{3}}C = O$$

(v) By alkaline hydrolysis of ester

$$\begin{array}{c} O \\ \parallel \\ R - C - O \\ R' + HO \\ R' + HO \\ Na(aq) \rightarrow \begin{array}{c} O \\ R - C - ONa \\ R - C - ONa \\ Alcohol \end{array} + \begin{array}{c} R'OH \\ Alcohol \end{array} .$$

(vi) From primary amines

$$CH_3CH_2NH_2 + HONO$$

 $\begin{array}{c} CH_{3}CH_{2}OH + N_{2} + H_{2}O \\ \\ \text{Ethanol} \end{array}$

□ It is not a good method of preparation of alcohols because number of by product are formed like alkyl chloride alkenes and ethers.

(vii) From Grignard reagent

(a) With oxygen :

Aminoethane

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

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

(b) With ethylene oxide :

$$R^{\delta^{-}} - Mg^{\delta^{+}} - X + \underbrace{\overset{\delta^{+}}{CH_{2}} - \overset{\delta^{+}}{CH_{2}}}_{O_{\delta^{-}}} \rightarrow$$

 $RCH_2CH_2 - OMgX \xrightarrow{H_2O} RCH_2CH_2OH + Mg(X)OH$ (c) With carbonyl compounds :

$$\overset{\delta^{-}}{R} \overset{\delta^{+}}{M} \overset{\delta^{+}}{R} - \overset{\delta^{+}}{M} \overset{H}{R} - \overset{H}{C} \overset{\delta^{+}}{\sigma} \overset{K^{+}}{R} \overset{H}{r} - \overset{H}{C} - \overset{H}{R} \overset{H}{\sigma} \overset{H}{\sigma} \overset{H}{R} \overset{H}{r} - \overset{H}{C} - \overset{H}{R} \overset{H}{\sigma} \overset{H}{\sigma}$$

 \Box If R' = H, product will be 1°alcohol.

 \Box If R' = R, product will be 2°alcohol.

□ If carbonyl compound is a ketone, product will be 3° alcohol.

□ It is the best method for preparation of alcohol because we can prepare every type of alcohols.

(viii) *The oxo process* : It is also called carbonylation or hydroformylation reaction. A mixture of alkene carbon monoxides and hydrogen. Under pressure and elevated temperature in the presence of catalyst forms aldehyde.

Catalyst is cobalt carbonyl hydride $[CoH(CO)_4]$ product is a mixture of isomeric straight chain (major) and branched chain (minor) aldehydes. Aldehydes are reduced catalytically to the corresponding alcohols.

$$2CH_3 - CH = CH_2 + 2CO + 2H_2 \rightarrow$$

OH (2) Physical properties of monohydric alcohols

(i) *Character* : Alcohols are neutral substances. These have no effect on litmus paper. This is analytical test for alcohols.

(ii) **Physical state :** The lower alcohols (upto C_{12}) are colourless alcohol with characteristic smell and burning taste. The higher members with more than 12-carbon atoms are colourless and odourless solids.

(iii) **Polar character :** Oxygen atom of the – OH group is more electronegative than both carbon and hydrogen. Thus the electron density near oxygen atom is slightly higher. Hydrogen bonding shown below

$$H - O - - - H - O - - - H - O - - - H - O$$
. This gives polar
 $\stackrel{|}{R}$ $\stackrel{|}{R}$ $\stackrel{|}{R}$ $\stackrel{|}{R}$ $\stackrel{|}{R}$

character to OH bond.

(iv) **Solubility** : The lower alcohols are miscible in water.

$$\begin{array}{c} H - O : \overset{\delta^{-}}{:} & \overset{\delta^{-}}{:} & \overset{\delta^{+}}{:} H - O : \text{ Solubility } \infty \xrightarrow{1} \\ & \overset{I}{\text{Size of alkyl groups}} \\ R & H \end{array}$$

Increase in carbon-chain increases organic part hence solubility in water decreases.

Isomeric 1°, 2°, 3° alcohols have solubility in order 1°> 2°> 3°.

(v) **Boiling points :** Due to intermolecular hydrogen bonding boiling points of alcohols are higher than hydrocarbon and ethers.

B.P. $\propto \frac{1}{\text{No. of branche s}}$; B.P. follows the trends :

1° alcohol > 2° alcohol > 3° alcohol

(vi) **Density** : Alcohols are lighter than water.

Density \propto Molecular masses.

(vii) *In toxicating effects* : Methanol is poisonous and is not good for drinking purposes. It may cause blindness and even death. Ethanol is used for drinking purposes.

(3) **Chemical properties :** Characteristic reaction of alcohol are the reaction of the – OH group. The reactions of the hydroxyl group consists of either cleavage of C - O bond or the cleavage of O - H bond.



C - O bond is weaker in the case of tertiary alcohols due to +I effect of alkyl groups while - OH bond is weaker in primary alcohols as electron density increase between O - H bond and hydrogen tends to separates as a proton.

$$\begin{array}{c} H \text{ weaker} \\ R \to \stackrel{|}{\underset{H}{\overset{}}} - O \stackrel{-}{-} H ; \\ H \\ Primary \end{array} \xrightarrow{R} CH - OH ; \\ R \xrightarrow{R} C \stackrel{-}{\underset{R}{\overset{}}} O - H \\ R \xrightarrow{\text{weaker}} \\ R \xrightarrow{\text{weaker}} \\ \text{Tertiary} \end{array}$$

Thus primary alcohols give the most of reaction by cleavage of O - H bond while tertiary alcohols are most reactive because of cleavage of C - O bond. Hence - O - H cleavage reactivity order : Primary > Secondary > Tertiary and C - O - cleavage reactivity order : Tertiary > Secondary > Primary alcohol

(i) Reaction involving cleavage of with removal of 'H' as proton

Alcohols are stronger acids than terminal acetylene but are not acidic enough to react with aqueous *NaOH* or *KOH*. Acidic nature is in the order $HOH > ROH > CH \equiv CH > NH_3 > RH$.

Acidic nature of alcohol decrease with increase of alkyl groups on – OH bonded carbon due to +I (inductive) effect of alkyl group.

 $2RO - H + 2M \rightarrow 2ROM + H_2 (M = Na, K, Mg, Al,$

etc.)

Evolution of H_2 shows the presence of -OH and reaction show that alcohols are acidic in nature. Alcohols acts as Bronsted acids because they donate a proton to a strong base (: B^-).

Example :

$$R - O - H + : B^{-} \rightarrow R - O : + B - H_{Conjugate acid}$$

(acid)
Alcohol
(acid)
 $Base$
Alkoxide
(conjugate base)

On reaction of alkoxide with water, starting alcohol is obtained.

This is the analytical test for alcohols.

(b) Reaction with carboxylic acid [Esterification]:

$$RCO - OH + H - OR'$$
 Conc. $RCOOR' + H_2O$

When *HCl* gas is used as catalyst, the reaction is called fischer-speier esterification.

Presence of bulky group in alcohol or in acid decreases the rate of esterification. This is due to steric hindrance of bulky group. Reactivity of alcohol in this reaction is $1^o > 2^o > 3^o$.

(c) *Reaction with acid derivatives* : (Analytical test of alcohol)

$$CH_{3} - C + Cl + H + O - CH_{2}CH_{3}$$
Ethanoyl chloride
$$\xrightarrow{Pyridine} CH_{3} - C - OCH_{2}CH_{3} + HCH_{3}$$
Ethylethanoate
(Ethylacetate)

Acylation :
$$CH_3 - \frac{O}{C - O - C - CH_3 + H} - OCH_2CH_3$$

 $\rightarrow CH_3 - \frac{O}{C - O - C - CH_3 + H} - OCH_2CH_3$
 $\rightarrow CH_3 - \frac{O}{C - OCH_2CH_3 + CH_3COOH}$
Ethylethanoate

(d) Reaction with grignard reagents :

$$\begin{array}{c} CH_3OH + \ C_2H_5MgBr \rightarrow C_2H_6 + CH_3OMgBr \\ Methyl \\ alcohol \\ br omide \\ \end{array} \xrightarrow{} Ethyl magnesium \\ br omide \\ \end{array}$$

(e) Reaction with ketene :

$$R - O - H + CH_{2} = C = O$$

$$\rightarrow CH_{2} = C - O - R \rightarrow CH_{3} - C - O - K$$

$$\downarrow H - O$$
(enol form)
(Keto form)

(f) Reaction with isocyanic acid :

$$R - \stackrel{\delta^{-}}{O} \stackrel{\delta^{+}}{H} + H - N = \stackrel{\delta^{+}}{\underset{\parallel}{C}} \rightarrow H - N = \stackrel{C}{C} - O - R$$
$$\stackrel{O}{\rightarrow} H - NH - \stackrel{C}{\underset{\parallel}{O}} O - R$$
$$\stackrel{O}{\rightarrow} H - NH - \stackrel{C}{\underset{\parallel}{O}} O - R$$
amino ester (Urethane)

(g) Reaction with ethylene oxide :

 $R - O - H + CH_{2} - CH_{2} \rightarrow CH_{2} - CH_{2} \xrightarrow{ROH} CH_{2} - CH_{2}$

(h) Reaction with diazomethane :

$$R - OH + CH_2N_2 \rightarrow R - O - CH_3 + N_2$$

(Ether)

(ii) Alkylation : $ROH + R'_2SO_4 \rightarrow ROR' + R'HSO_4$

(iii) Reaction involving cleavage of -C - OH with

removal or substitution of -OH group

(a) Reaction with hydrogen halides : Alcohols give alkyl halide. The reactivity of *HX* is in the order of *HI* > *HBr* > *HCl* and the reactivity of *ROH* is in the order of benzyl > allyl > 3° > 2° > 1° . The reaction follows a nucleophilic substitution mechanism.

Grove's process

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

If alcohols react with *HI* and red phosphorus, alkane will be formed.

$$C_2H_5OH + 2HI \xrightarrow{\text{Red }P} C_2H_6 + I_2 + H_2O$$

Primary alcohols follow S_{N^2} mechanism.

$$\begin{array}{c} R - OH_2^+ + X^- \rightarrow {}^{\delta^-}X - - R - - OH_2^{\delta^+} \rightarrow R - X + H_2O \\ \text{Protonated} \\ 1^\circ \text{ alcohol} \end{array}$$

In secondary and tertiary alcohols, the S_{M^1} mechanism operates

$$R - OH \stackrel{\underline{H^+}}{\longleftarrow} R - OH \stackrel{\underline{+}^-H_2O_*}{\underbrace{\longrightarrow}} R^+ \stackrel{\underline{X^-}}{\longrightarrow} R - X$$

(b) *Reaction with PCl*₅ :

 $ROH + PX_5 \rightarrow RX + POX_3 + HX$; X = Cl (Analytical test for alcohols)

(c) Reaction with PCl₃:

$$\begin{array}{lll} 3ROH \\ {}_{Alcohol} \end{array} + \begin{array}{l} PCl_3 \\ {}_{Phosphorus} \\ {}_{trichloride} \end{array} \rightarrow \begin{array}{l} 3RCl + H_3PO_3 \\ {}_{Alky1} \\ {}_{phosphorus} \\ {}_{acid} \end{array}$$

(d) Reaction with thionyl chloride [SOCl₂]:

 $ROH + SOCl_2 \xrightarrow{\text{Pyridine}} RCl + SO_2 + HCl$

(e) Reaction with ammonia :

$$ROH + NH_3 \xrightarrow{Al_2O_3} RNH_2$$

 $360^{\circ}C \xrightarrow{RnH_2}$ Primary

 $\begin{array}{c} ROH \\ \hline Al_2O_3 \end{array} \xrightarrow{R_2} NH \xrightarrow{ROH} \xrightarrow{ROH} R_3N \\ \text{Secondary} \\ amine \end{array} \xrightarrow{Al_2O_3} \begin{array}{c} R_3N \\ \text{Tertiary} \\ \text{amine} \end{array}$

(f) Reaction with HNO₃ :

$$R - OH + \text{conc. } HNO_3 \rightarrow R - O - N \bigcirc O + H_2O$$

alkyl nitrate

(g) Reaction with H_2SO_4 [Dehydration of alcohol] : The elimination of water from a compound is known as dehydration. The order of ease dehydration is Tertiary > Secondary > primary alcohol. The products of dehydration of alcohols are depend upon the nature of dehydrating agents and temperature.



Alcohol leading to conjugated alkene are dehydrated to a greater extent than those of alcohols leading to nonconjugated alkene. Thus dehydration is in order



(iv) General reaction of alcohols

(a) Reduction : $R - OH + 2HI \xrightarrow{\Delta} R - H + H_2O + I_2$

(b) Oxidation : Difference between 1°, 2° and 3° alcohols.

$$1^{\circ} \rightarrow RCH_{2}OH \rightarrow R - C = O \rightarrow R - C = O$$

$$H \qquad OH$$
Aldehy de Carboxy lic acid
$$2^{\circ} \rightarrow R - CH - R' \xrightarrow{CrO_{3}} R - C - R'$$

$$OH \qquad O$$
Secondary alcohol
$$\xrightarrow{O} RCOOH + CO_{2} + H_{2}O$$

$$3^{\circ} \rightarrow CH_{3} - \overset{I}{C} - OH \xrightarrow{4[O]} CH_{3} - \overset{I}{C} = O$$

$$CH_{3} \qquad CH_{3} - \overset{I}{C} - OH \xrightarrow{4[O]} CH_{3} - \overset{I}{C} = O$$

$$CH_{3} \qquad CH_{3} - \overset{I}{C} - OH \xrightarrow{4[O]} CH_{3} - \overset{I}{C} = O$$

$$CH_{3} \qquad CH_{3} - \overset{I}{C} - OH \xrightarrow{4[O]} CH_{3} - \overset{I}{C} = O$$

$$CH_{3} \qquad CH_{3} - \overset{I}{C} - OH \xrightarrow{4[O]} CH_{3} - \overset{I}{C} = O$$

$$CH_{3} \qquad CH_{3} - \overset{I}{C} - OH \xrightarrow{4[O]} CH_{3} - \overset{I}{C} = O$$

$$CH_{3} \qquad CH_{3} - \overset{I}{C} - OH \xrightarrow{4[O]} CH_{3} - \overset{I}{C} = O$$

$$CH_{3} \qquad CH_{3} - \overset{I}{C} = O$$

$$CH_{3} \qquad CH_{3} - \overset{I}{C} = O$$

$$CH_{3} \qquad CH_{3} - \overset{I}{C} = O$$

$$CH_{3} - O$$

$$CH_{3}$$

 $\hfill\square$ 3° alcohols are resistant to oxidation, but on taking stronger oxidising agent they form ketone.

(c) Catalytic oxidation/dehydrogenation



$$3^{\circ} CH_{3} \xrightarrow[CH_{3}]{CH_{3}} CH_{3} \xrightarrow[CH_{3}]{CH_{3}} CH_{3} \xrightarrow[CH_{3}]{CH_{3}} CH_{3} \xrightarrow[CH_{3}]{CH_{2}} CH_{3} \xrightarrow[CH_{3}]{CH_{2}} CH_{2} \xrightarrow[Alkene]{CH_{3}} CH_{3} CH_{3}$$

Important reagents used for oxidation of alcohols

• PCC [Pyridinium chloro chromate $(C_6H_5 \overset{\oplus}{N}HClCrO_3^{-})$] to oxidise 1° alcohols to aldehydes and 2° alcohols to ketones.

• PDC [Pyridinium di chromate $(C_5H_5.NH)_2^{2+}Cr_2O_7^{2-}$] to oxidise 1° alcohols to aldehyde and 2° alcohol to ketones.

• $H_2 CrO_4$ (chromic acid) to oxidise 1° alcohol to carboxylic acid.

• $CrO_3 \cdot H_2SO_4$ / Acetone to oxidise 2° alcohol to ketones.

• Jones reagents (chromic acid in aqueous acetone solution) oxidise 1° alcohol to aldehyde and 2° alcohol to ketone without affecting (C = C) double bond.

• MnO_2 selectively oxidises the -OH group of allylic and benzylic 1° and 2° alcohols to give aldehyde and ketone respectively.

• N_2O_4 in $CHCl_3$ oxidises primary and secondary benzyl alcohol.

(e) Reaction with cerric ammonium nitrate : Cerric ammonium nitrate + $ROH \rightarrow$ Red colour solution of

complex. This is analytical test for alcohols.

(f) *Iodoform test* : When a few drops of alcohol are warmed with iodine and *NaOH* yellow precipitate of iodoform with characteristic smell is obtained. Any alcohol consists CH_3CHOH group give iodoform test.

Since reaction takes place with alkali solution as one of the reagents hence alkyl halide like $CH_3 - CH_2Cl$ and $CH_3 - CH - R$ will also give this test.

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(4) Uses of monohydric alcohol :

(i) Uses of ethanol : It is used

(a) In alcoholic beverages, (b) As a solvent in paints, varnishes, oils, perfumes etc., (c) In the preparation of chemical like chloroform, ether etc., (d) As a fuel in spirit lamps, (e) As an antifreeze for automobile radiators, (f) In the scientific apparatus like spirit levels, (g) As power alcohol.

(ii) Uses of methanol :

(a) Methanol is an important industrial starting material for preparing formaldehyde, acetic acid and other chemicals.

(b) As a fuel (a petrol substitute). A 20% mixture of methyl alcohol and gasoline is a good motor fuel.

(c) As an antifreeze or automobile radiators.

(d) To denature ethyl alcohol. The mixture is called methylated spirit.

(e) In the preparation of dyes, medicines and perfumes. Methyl salicylate and methyl anthra anilate are used in perfumery.

Methanol	Ethanol
(i) When CH_3OH is heated on	(i) It does not give
Cu coil it gives formalin like	formalin like smell.
smell.	
(ii) When CH_3OH is heated	(ii) No such odour is
with salicylic acid in H_2SO_4	given.
(conc.) then methyl salicylate	
is formed which has odour	
like winter green oil.	
(iii) It does not give haloform	(iii) It gives
or iodoform test.	haloform test

Interconversion of monohydric alcohols

(i) Primary alcohol into secondary alcohols

$$C_{3}H_{7}OH \xrightarrow{SOC_{2}} C_{3}H_{7}Cl \xrightarrow{\text{alc KOH}} CH_{3}CH = CH_{2}$$
Propan-1-ol
(1° alcohol)
$$\xrightarrow{HBr} CH_{3}CH CH_{3} \xrightarrow{\text{aq. KOH}} CH_{3}CH CH_{3}$$
Br
$$\xrightarrow{OH}$$
Propan-2-ol
(2° alcohol)

(ii) Secondary alcohol into tertiary alcohol

colour)

Tertiary

 $\begin{array}{c} OH & O \\ CH_{3} - CH - CH_{3} & \overbrace{K_{2}Cr_{2}O_{7}/H^{+}}^{[O]} CH_{3} - C - CH_{3} \\ Propan-2-ol \\ (Iso-propy | alcohol) \\ (2^{\circ} alcohol) \\ \hline \end{array} \xrightarrow{(H_{3}MgBr} CH_{3} - \bigvee_{i}^{[C]} - CH_{3} \xrightarrow{H^{+}, H_{2}O} CH_{3} - \bigvee_{i}^{[C]} - CH_{3} \\ \hline \end{array} \xrightarrow{(H_{3}MgBr} CH_{3} \xrightarrow{(C_{1}-C_{1})} CH_{3}$

(iii) Primary alcohol into tertiary alcohol

$$\begin{array}{c} CH_{3} & CH_{3} \\ \downarrow \\ CH_{3} CH CH_{2} OH \xrightarrow{H_{2}SO_{4}, \text{Heat}} CH_{3} - C = CH_{2} \xrightarrow{HBr} \\ \xrightarrow{2-\text{Methy lpropan-1-ol}(1^{\circ})} & \text{Dehy dration} \end{array} \xrightarrow{CH_{3}} CH_{3} - C = CH_{2} \xrightarrow{HBr} \\ \xrightarrow{HBr} \\ \xrightarrow{\text{Markowniko ffs}} \\ \xrightarrow{\text{rule}} CH_{3} - C = CH_{2} \xrightarrow{HBr} \\ \xrightarrow{HBr}$$

$$CH_{3} \xrightarrow[]{} CH_{3} \xrightarrow[]{} CH_$$

(iv) *Lower alcohol into higher alcohol* (ascent of series)

$$\begin{array}{c} CH_{3}OH \xrightarrow{HI} CH_{3}I \xrightarrow{KCN} CH_{3}CN \\ \xrightarrow{\text{Methanol}} 1 \text{ carbon atom} \end{array} \xrightarrow{4(H)} CH_{3}CH_{2}NH_{2} \xrightarrow{HONO} CH_{3}CH_{2}OH \\ \xrightarrow{\text{Reduction}} CH_{3}CH_{2}NH_{2} \xrightarrow{HONO} CH_{3}CH_{2}OH \\ \xrightarrow{\text{Ethanol}} (2 \text{ carbon atoms}) \end{array}$$

(v) *Higher alcohol into lower alcohol* [Descent series]

NO

Distinguish between primary, secondary and tertiary monohydric alcohols

(i) *Lucas test* : A mixture of anhydrous *ZnCl*₂ + conc. *HCl* is called as Lucas reagent.

Primary	$R - CH_2 - OH \xrightarrow{\text{conc. } HCl / ZnCl_2 \text{ anhy.}} R - CH_2 - Cl \rightarrow \text{ ppt. appears after heating}$			
Secondary	$R_2CH - OH \xrightarrow{\text{conc. } HCl / ZnCl_2 \text{ anhy.}}_{-H_2O} R_2 - CH - Cl \rightarrow \text{ ppt. appears with in 5 minutes}$			
Tertiary	$R_3C - OH \xrightarrow{ZnCl_2/HCl} R_3C - Cl \rightarrow \text{ppt. appears immediately}$			
(ii) Victor mayer test : Also known as RBW test. RBW \rightarrow Red, Blue, White test.				
(ii) Victor ma	ayer test : Also known as RBW test. RBW \rightarrow Red, Blue, White test.			
(ii) Victor ma Primary	$\begin{array}{c} \textbf{ayer test}: \text{Also known as RBW test. RBW} \rightarrow \text{Red, Blue, White test.} \\ \hline C_2H_5OH \xrightarrow{P+I_2} C_2H_5I \xrightarrow{AgNO_2} C_2H_5NO_2 \xrightarrow{HONO} CH_3 \xrightarrow{-C-NO_2} \xrightarrow{NaOH} CH_3 \xrightarrow{-C-NO_2} \\ & \parallel \\ NOH \\ & \text{Nitrolic acid} \end{array} \xrightarrow{O-NO_2} \xrightarrow{NONa} \\ \hline Sod. \text{ salt of nitrolic acid (Red colour)} \end{array}$			

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 $(CH_3)_3COH \xrightarrow{P+I_2} (CH_3)_3Cl \xrightarrow{AgNO_2} (CH_3)_3CNO_2 \xrightarrow{HONO}$ No reaction (colourless)

H

Dihydric alcohols

These are compound containing two hydroxyl groups. These are dihydroxy derivatives of alkanes. Their general formula is $C_n H_{2n+2}O_2$. The simplest and most important dihydric alcohol is ethylene glycol. They are classified as α , β , γ glycols, according to the relative position of two hydroxyl groups. α is 1, 2 glycol, β is 1, 3 glycol.

(1) **Preparation**

(i) *From ethylene* : (a) Through cold dilute alkaline solution of Bayer's reagent



(b) With O_2 in presence of Ag :

$$\begin{array}{c} CH_{2} \\ || \\ CH_{2} \\ CH_{2} \end{array} + \frac{1}{2} O_{2} \xrightarrow[Ag,200-400^{\circ}C]{} CH_{2} \\ | \\ Ag,200-400^{\circ}C \\ CH_{2} \end{array} \rightarrow O \xrightarrow[H_{2}O]{} H_{2}O \\ | \\ CH_{2}OH \\$$

(c) *With HOCl followed by hydrolysis* : (Industrial method)

 $\begin{array}{c} CH_{2} & CH_{2}OH \\ || \\ CH_{2} & +HOCl \rightarrow & | \\ CH_{2}Cl \\ \text{Ethy lene chlorohy drin} \\ \hline \\ & \underbrace{NaHCO_{3}}_{CH_{2}OH} + NaCl + CO_{2} \\ \hline \\ & CH_{2}OH \\ \hline \\ & Glycol \end{array}$

(ii) From 1, 2 dibromo ethane [Lab method]: $CH_{2}Br + Na_{2}CO_{3} + H_{2}O \rightarrow | + 2NaBr + CO_{2}$ $CH_{2}Br + 2CH_{3}COOK \xrightarrow{CH_{3}COOH} -2KBr + CH_{2}OOCCH_{3}$ $CH_{2}Br + 2CH_{3}COOK \xrightarrow{CH_{3}COOH} -2KBr + CH_{2}OOCCH_{3}$ $CH_{2}OOCCH_{3}$ $CH_{2}OH + 2CH_{3}COONa$

(2) Physical properties

(i) It is a colourless, syrupy liquid and sweet in taste. Its boiling point is $197^{\circ}C$.

(ii) It is miscible in water and ethanol in all proportions but is insoluble in ether.

(iii) It is toxic as methanol when taken orally.

(iv) It is widely used as a solvent and as an antifreeze agent.

(3) Chemical properties



Chlorohydrin

Dioxalane formation provides a path of protecting a carbonyl group in reaction studied in basic medium in which acetals are not affected. The carbonyl compound may be regenerated by the addition of periodic acid to aqueous solution of the dioxalane or by acidic hydrolysis.

$$\begin{array}{c|c} R \\ R \\ \hline R \\ \hline C = O + \begin{array}{|} CH_{2}OH \\ CH_{2}OH \\ \hline CH_{2}OH \\ \hline R \\ \hline \end{array} \begin{array}{c} R \\ \hline C \\ \hline O \\ \hline O \\ - CH_{2} \\ \hline O \\ - CH_{2} \\ \hline O \\ - CH_{2} \\ \hline \end{array} \begin{array}{c} HIO_{4} \\ \hline O \\ - CH \\ - CO \\ - R \\ - 2HCHO \\ \hline \end{array} \end{array}$$

Aldehyde is more reactive than ketone in dioxalane formation.



(4) Uses

(i) Used as an antifreeze in car radiators.

(ii) Used in the manufacture of dacron, dioxane etc.

(iii) As a solvent and as a preservatives.

(iv) As a cooling agent in aeroplanes.

(v) As an explosives in the form of dinitrate.

Trihydric alcohols.

600°C

 CH_2

Ally khloride

 CH_2

propene

The only important trihydric alcohol is glycerol (propane-1, 2, 3-triol). It occurs as glycosides in almost all animal and vegetable oils and fats.

(1) Preparation (i) From oils and fats CH_2OOCR CH_2OH $CH OOCR + 3H_2O \rightarrow CH OH + 3RCOOH$ CH₂OOCR CH_2OH Oil or fat Glycerol CH2OOCR NaOH $CH_{2}OH$ Hy droly sis CH OOCR + NaOH - $\rightarrow CH OH$ 3RCOONa + Sodium salt of higher fatty acids CH₂OOCR NaOH CH ,OH Oil or fat (ii) By fermentation of sugar $\xrightarrow{\text{Yeast}} C_3H_8O_3 + CH_3CHO + CO_2$ $C_6 H_{12} O_6$ -Na₂SO₃ Glucose Glycerol Acetaldehyde (iii) From propene [Modern method] CH_3 CH_2Cl CH_2OH NaOH (dil) Cl_2 CHCH $\rightarrow CH$

 CH_2

Ally lalcohol

$$\xrightarrow{HOCl} \begin{array}{c} CH_2OH & CH_2-OH \\ \hline HOCl & CH_2-OH \\ CH_2-OH \\ \beta-\text{monochloro hydrin} \end{array} \xrightarrow{I} \begin{array}{c} CH_2-OH \\ \hline CH_2-OH \\ Gly \text{ cerol} \end{array}$$

(iv) From propenal :

$$CH_{2} = CHCHO \xrightarrow{H_{2}} CH_{2} = CHCH_{2}OH$$
$$\xrightarrow{H_{2}O_{2}/OH} HOCH_{2}CHOHCH_{2}OH$$
Glycerol

(2) Physical properties

(i) It is a colourless, odourless, viscous and hygroscopic liquid.

(ii) It has high boiling point *i.e.*, 290°C. The high viscosity and high boiling point of glycerol are due to association through hydrogen bonding.

(iii) It is soluble in water and ethyl alcohol but insoluble in ether.

(iv) It is sweet in taste and non toxic in nature.

(3) Chemical properties

(i) **Reaction with sodium**

 $CH_2 - OH$ CH₂ONa CH₂ONa Na Na CH - OH -CH - OHCH - OHRoom Room $CH_2 - OH$ temperature CH2-OH temperature CH ONa Monosodium glycerol Disodium gly cerolate (ii) Reaction with PCl₅, PBr₃ and PI₃ $CH_{2}OH$ $CH_{2}Cl$ (a) $CH OH + 3PCl_5$ $+ 3POCl_3 + 3HCl$ CH Cl CH 20H CH₂Cl Gly cery l **t**ichloride (1, 2, 3-Trichloropropane) CH_2OH $CH_{2}Br$ (b) *CH OH* $+ PBr_3$ $CH Br + H_3 PO_3$ \rightarrow CH ,OH ĊH₂Br 1, 2, 3-Tribromopropane $CH_{2}OH$ $CH_{2}I$ CH_{2} CH I (c) *CH OH* + $PI_2 \rightarrow$ CH $+ I_2$ CH ,OH CH₂I $\dot{C}H_2I$ Ally liodide (Unstable) (iii) Reaction with HCl or HBr $CH_{2}OH$ $CH_{2}Cl$ CH_2OH 110°C CH OH CH Cl CH OH + -> +HCl CH_2OH CH_2OH CH_2OH α -Gly cerol monochloro hy drin (66%) β -Glycerol monochloro hydrin (34%) CH_2Cl $CH_{2}Cl$ Excess of HCl CH OH CH Cl $110^{\circ} C$ CH,OH CH ,Cl Gly cerol α, β -dichlorohy drin Glycerol α, α' -dichlorohy drin (56%)(44%)

(iv) Reaction with HI



 $2HIO_{2} \pm H_{2}O_{3}$

(viii) Reaction with nitric acid

 $\begin{array}{c} CH_2OH & CH_2ONO_2 \\ CHOH + 3HNO_3 \xrightarrow{\text{conc.}H_2SO_4} & CHONO_2 + 3H_2O \\ CH_2OH & CH_2ONO_2 \\ Gly cervl initrate (T.N.G.) \end{array}$

Dynamite is prepared from T.N.G.

Dynamite : A mixture of T.N.G. and glyceryl dinitrate absorbed in kieselguhr is called dynamite. It was discovered by Alfred. Nobel in 1867. It releases large volume of gases and occupy 10,900 times the volume of nitroglycerine.

$$C_3H_5(ONO)_3 \rightarrow 12CO_2 + 10H_2O + 6N_2 + O_2$$

Blasting gelatin : A mixture of glyceryl trinitrate and cellulose nitrate (gun cotton).

Cordite : It is obtained by mixing glyceryl trinitrate with gun cotton and vaseline it is smokeless explosive.

(4) **Uses**

(a) As antifreeze in automobile radiator.

(b) In the preparation of good quality of soaphand lotions shaving creams and tooth pastes.

(c) As a lubricant in watches.

(d) As a preservatives.

(e) As a sweetening agent in confectionary, beverages and medicines being non toxic in nature.

(f) In manufacture of explosives such as dynamite.

(5) Analytical tests of glycerol

(i) **Acrolein test**: When glycerol is heated with $KHSO_4$ a very offensive smell is produced due to formation of acrolein. Its aqueous solution restores the colour of schiff's reagent and reduces Fehling solution and Tollen's reagent.

(ii) **Dunstan's test**: A drop of phenolphthalein is added approximately 5 *ml* of borax solution. The pink colour appears on adding 2-3 drops of glycerol, pink colour disappears. The pink colour appears on heating and disappears on cooling again.

Unsaturated alcohols (Allyl alcohol)

(1) Preparation

(i) From allyl halide

$$CH_2 = CH - CH_2Br + H_2O \rightarrow CH_2 = CH - CH_2OH + HBr$$

Allykalcohol

(ii) By heating glycerol with oxalic acid :

CH_2OH	CH_2OOC	CH_2
HOOC	$-2H_2O$, $CUOOC$	Heat Heat
HOOC		$-2CO_2$
CH ₂ OH	CH_2OH	CH ₂ OH
-	-	Allylalcohol

(2) Physical properties

(a) It is colourless, pungent smelling liquid.

(b) It is soluble in water, alcohol and ether in all proportion.

(3) Chemical properties



Phenol (Carbolic acid), C₆H₅OH or Hydroxy benzene

It was discovered by Runge in the middle oil fraction of coal-tar distillation and named it 'carbolic acid' (carbo = coal, oleum = oil) or phenol containing 5% water is liquid at room temperature and is termed

as carbolic acid. It is also present in traces in human urine.

(1) **Preparation**

Sodium benzene sulphonate

(i) From benzene sulphonic acid

$$\begin{array}{ccc} C_{6}H_{6} & \xrightarrow{H_{2}SO_{4}(\text{fuming})} & C_{6}H_{5}SO_{3}H & \xrightarrow{NaOH} \\ \text{Benzene} & \text{Benzene sulphonic acid} \\ \end{array}$$

$$\begin{array}{cccc} C_{6}H_{5}SO_{3}Na & \xrightarrow{NaOH} & C_{6}H_{5}ONa & \xrightarrow{H^{+}/H_{2}O} & C_{6}H_{5}OH \\ \text{m benzene sulphonate} & \xrightarrow{Sodium phenoxide} & \xrightarrow{\text{or } CO_{2}/H_{2}O} & Phenol \end{array}$$

This is one of the laboratory methods for the preparation of phenol. Similarly methyl phenols (cresols) can be prepared.



(ii) From benzene diazonium chloride



Diazonium salts are obtained from aniline and its derivatives by a process called diazotisation.

(iii) From Grignard reagent

(iv) From salicylic acid :



(v) Middle oil of coal tar distillation : Middle oil of coal-tar distillation has naphthalene and phenolic compounds. Phenolic compounds are isolated in following steps.

Step I : Middle oil is washed with H_2SO_4 . It dissolves basic impurities like pyridine (base).

Step II : Ecessive cooling separates naphthalene (a low melting solid)

Step III : Filtrate of step II is treated with aqueous *NaOH* when phenols dissolve as phenoxides. Carbon dioxide is then blown through the solution to liberate phenols.

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$$

$$\xrightarrow{CO_2, H_2O} C_6H_5OH + Na_2CO_3$$

Step IV : Crude phenol (of step III) is subjected to fractional distillation.

 $\xrightarrow{180^{\circ}C} \rightarrow o, m, p\text{-cresols}$

Crude

→ xylols (hydroxy

(vi) Raschig's process

fraction

distillati

$$C_{6}H_{6} + HCl + \frac{1}{2}O_{2} \xrightarrow{CuCl_{2}/FeCl_{3}}{250^{\circ}C} \xrightarrow{C_{6}H_{5}Cl} H_{2}O_{1}$$
Benzene

$$C_{6}H_{5}Cl + H_{2}O \xrightarrow{425^{\circ}C} C_{6}H_{5}OH + HCl$$

Discrete steam Phenol

(vii) Dow process

$$C_{6}H_{5}Cl + 2NaOH \xrightarrow{300^{\circ}C} H_{5}ONa + NaCl + H_{2}O$$

Chlorobenz ene

sodium phenoxide on treatment with mineral acid yields phenol.

 $2C_6H_5ONa + H_2SO_4 \rightarrow 2C_6H_5OH + Na_2SO_4$

(viii) Oxidation of benzene

$$2C_6H_6 + O_2 \xrightarrow{V_2O_5} 2C_6H_5OH$$

(ix) Oxidation of isopropyl benzene [Cumene]



(2) **Physical properties**

(i) Phenol is a colourless crystalline, deliquescent solid. It attains pink colour on exposure to air and light.

(ii) They are capable of forming intermolecular *H*bonding among themselves and with water. Thus, they have high boiling points and they are soluble in water.





(crossed intermolecular *H*-bonding between water and phenol molecules)

Due to intermolecular *H*- bonding and high dipole moment, melting points and boiling points of phenol are much higher than that of hydrocarbon of comparable molecular weights.

(iii) It has a peculiar characteristic smell and a strong corrosive action on skin.

(iv) It is sparingly soluble in water but readily soluble in organic solvents such as alcohol, benzene and ether.

(v) It is poisonous in nature but acts as antiseptic and disinfectant.

(3) Chemical properties

(i) *Acidic nature* : Phenol is a weak acid. The acidic nature of phenol is due to the formation of stable phenoxide ion in solution.

$$C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^- + H_3O^+$$

Phenoxide ion

The phenoxide ion is stable due to resonance.



The negative charge is spread throughout the benzene ring. This charge delocalisation is a stabilising factor in the phenoxide ion and increase acidity of phenol. [No resonance is possible in alkoxide ions (RO^{-}) derived from alcohols. The negative charge is localised on oxygen atom. Thus alcohols are not acidic].

□ Phenols are much more acidic than alcohols but less so than carboxylic acids or even carbonic acid. This is indicated by the values of ionisation constants. The relative acidity follows the following order

$$\begin{array}{c} K_{a}({\rm approx.}) & (10^{-5}) \\ RCOOH \\ Carboxylic acid \end{array} > \begin{array}{c} (10^{-7}) > (10^{-10}) > (10^{-14}) > (10^{-18}) \\ H_{2}CO_{3} \\ C_{6}H_{5}OH \\ Phenol \end{array} > \begin{array}{c} (10^{-14}) > (10^{-18}) \\ HOH \\ Water \\ Alcohols \end{array}$$

Effects of substituents on the acidity of phenols

: Presence of electron attracting group, (e.g., $-NO_2$, -

X, $-NR_3^+$, -CN, -CHO, -COOH) on the benzene ring increases the acidity of phenol as it enables the ring to draw more electrons from the phenoxy oxygen and thus releasing easily the proton. Further, the particular effect is more when the substituent is present on *o*- or *p*-position than in *m*-position to the phenolic group.

The relative strengths of some phenols (as acids) are as follows :

p-Nitrophenol > o-Nitrophenol > m- Nitrophenol > Phenol

Presence of electron releasing group, (e.g., $-CH_3$, $-C_2H_5$, $-OCH_3$, $-NR_2$) on the benzene ring decreases the acidity of phenol as it strengthens the negative charge on phenoxy oxygen and thus proton release becomes difficult. Thus, cresols are less acidic than phenol.

However, *m*-methoxy and *m*-aminophenols are stronger acids than phenol because of -I effect and absence of +R effect.

m-methoxy phenol > *m*-amino phenol > phenol > *o*-methoxy phenol > *p*-methoxy phenol

Chloro phenols : o > m > p-

Cresols : m - > p - > o -

Dihydric phenol : m - > p - > o-

The acidic nature of phenol is observed in the following :

(a) Phenol changes blue litmus to red.

(b) Highly electropositive metals react with phenol. $2C_6H_5OH + 2Na \rightarrow 2C_6H_5ONa + H_2$

(c) Phenol reacts with strong alkalies to form phenoxides. $C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$

However, phenol does not decompose sodium carbonate or sodium bicarbonate, *i.e.*, CO_2 is not evolved because phenol is weaker than carbonic acid.

(ii) Reactions of -OH group

(a) Reaction with $FeCl_3$: Phenol gives violet colouration with ferric chloride solution (neutral) due to the formation of a coloured iron complex, which is a characteristic to the existence of keto-enol tautomerism in phenols (predominantly enolic form).



This is the test of phenol.

(b) *Ether formation* : Phenol reacts with alkyl halides in alkali solution to form phenyl ethers (Williamson's synthesis). The phenoxide ion is a nucleophile and will replace halogenation of alkyl halide.

$$\begin{split} C_{6}H_{5}OH + NaOH &\rightarrow C_{6}H_{5}ONa + H_{2}O\\ \text{Sod. phenoxide} \\ C_{6}H_{5}ONa + ClCH_{3} &\rightarrow C_{6}H_{5}OCH_{3} + NaCl\\ C_{6}H_{5}OK + lC_{2}H_{5} &\rightarrow C_{6}H_{5} - O - C_{2}H_{5} + Kl\\ \text{Ethoxy benzene (Phenetol)} \\ C_{6}H_{5}ONa + Cl - HC(CH_{3})_{2} &\rightarrow C_{6}H_{5} - O - HC(CH_{3})_{2}\\ \text{Isopropy 1 chloride} \\ \end{split}$$

Ethers are also formed when vapours of phenol and an alcohol are heated over thoria (ThO_2) or Al_2O_3 .

$$C_6H_5OH + HOCH_3 \xrightarrow{\Delta, ThO_2} C_6H_5 - O - CH_{Methoxy benzene}$$

(c) *Ester formation* : Phenol reacts with acid chlorides (or acid anhydrides) in alkali solution to form phenylesters (Acylation). This reaction (Benzoylation) is called **Schotten-Baumann** reaction.

$$C_{6}H_{5}OH + NaOH \rightarrow C_{6}H_{5}ONa + H_{2}O$$

$$O$$

$$C_{6}H_{5}ONa + Cl C CH_{3} \rightarrow C_{6}H_{5}OOCCH_{3} + NaCl$$
Sodium phenoxide Acety khloride Phenyl acetate
$$C_{6}H_{5}OH + (CH_{3}CO)_{2}O \xrightarrow{NaOH} Acetic anhydride}$$

$$C_{6}H_{5}OH + (CH_{3}CO)_{2}O \xrightarrow{NaOH} Phenyl acetate (ester)$$

$$O$$

$$C_{6}H_{5}OH + Cl Cl C - C_{6}H_{5} \xrightarrow{NaOH} Benzoyl chloride}$$

$$O$$

$$C_{6}H_{5}OH + Cl Cl C - C_{6}H_{5} \xrightarrow{NaOH} Phenyl acetate (ester)$$

$$O$$

$$C_{6}H_{5}OH + Cl Cl C - C_{6}H_{5} \xrightarrow{NaOH} Phenyl acetate (ester)$$

$$O$$

$$C_{6}H_{5}OH + Cl Cl C - C_{6}H_{5} \xrightarrow{NaOH} Phenyl acetate (ester)$$

$$O$$

$$C_{6}H_{5}OH + Cl Cl C - C_{6}H_{5} \xrightarrow{NaOH} Phenyl acetate (ester)$$

$$O$$

$$C_{6}H_{5}OH + Cl Cl C - C_{6}H_{5} \xrightarrow{NaOH} Phenyl acetate (ester)$$

$$O$$

$$C_{6}H_{5}OH + Cl Cl C - C_{6}H_{5} \xrightarrow{NaOH} Phenyl acetate (ester)$$

$$O$$

$$C_{6}H_{5}OH + Cl Cl C - C_{6}H_{5} \xrightarrow{NaOH} Phenyl acetate (ester)$$

$$O$$

$$C_{6}H_{5}OH + Cl Cl C - C_{6}H_{5} \xrightarrow{NaOH} Phenyl acetate (ester)$$

$$O$$

$$C_{6}H_{5}OH + Cl Cl C - C_{6}H_{5} \xrightarrow{NaOH} Phenyl acetate (ester)$$

$$O$$

$$C_{6}H_{5}OH + Cl Cl C - C_{6}H_{5} \xrightarrow{NaOH} Phenyl acetate (ester)$$

$$O$$

$$C_{6}H_{5}OH + Cl Cl C - C_{6}H_{5} \xrightarrow{NaOH} Phenyl acetate (ester)$$

$$O$$

$$C_{6}H_{5}OH + Cl Cl C - C_{6}H_{5} \xrightarrow{NaOH} Phenyl acetate (ester)$$

$$O$$

$$C_{6}H_{5}OH + Cl Cl C - C_{6}H_{5} \xrightarrow{NaOH} Phenyl acetate (ester)$$

$$O$$

$$C_{6}H_{5}OH + Cl Cl C - C_{6}H_{5} \xrightarrow{NaOH} Phenyl acetate (ester)$$

$$O$$

$$C_{6}H_{5}OH + Cl Cl C - C_{6}H_{5} \xrightarrow{NaOH} \xrightarrow{NaOH} Phenyl acetate (ester)$$

$$O$$

$$C_{6}H_{5}OH + Cl Cl C - C_{6}H_{5} \xrightarrow{NaOH} \xrightarrow$$

The phenyl esters on treatment with anhydrous *AlCl*₃ undergoes **Fries rearrangement** to give *o*- and *p*-hydroxy ketones.



(d) Reaction with PCl_5 : Phenol reacts with PCl_5 to form chlorobenzene. The yield of chlorobenzene is poor and mainly triphenyl phosphate is formed.

$$C_6H_5OH + PCl_5 \rightarrow C_6H_5Cl + POCl_3 + HCl_3$$

$$3C_6H_5OH + POCl_3 \rightarrow (C_6H_5)_3PO_4 + 3HCl$$

(e) *Reaction with zinc dust* : When phenol is distilled with zinc dust, benzene is obtained.

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

(f) Reaction with ammonia : Phenol reacts with ammonia in presence of anhydrous zinc chloride at $300^{\circ}C$ or $(NH_4)_2SO_3/NH_3$ at $150^{\circ}C$ to form aniline. This conversion of phenol into aniline is called **Bucherer reaction.**

$$C_6H_5OH + NH_3 \xrightarrow{ZnCl_2} C_6H_5NH_2 + H_2O$$

 $\xrightarrow{300^{\,o}C} C_6H_5NH_2 + H_2O$

(g) Action of P_2S_5 : By heating phenol with phosphorus penta sulphide, thiophenols are formed.

$$5C_6H_5OH + P_2S_5 \rightarrow 5C_6H_5SH + P_2O_5$$

Thiophenol

(iii) **Reactions of benzene nucleus :** The -OH group is *ortho* and *para* directing. It activates the benzene nucleus.

(a) *Halogenation* : Phenol reacts with bromine in carbon disulphide (or $CHCl_3$) at low temperature to form mixture of *ortho* and *para* bromophenol.



Phenol forms a white precipitate with excess of bromine water yielding 2, 4, 6-tribromophenol.

(b) Sulphonation : Phenol reacts with conc. H_2SO_4 readily to form mixture of ortho and para hydroxy benzene sulphonic acids.



At low temperature $(25^{\circ}C)$, the *ortho*-isomer is the major product, whereas at $100^{\circ}C$, it gives mainly the *para*-isomer.

(c) Nitration : Phenol reacts with dilute nitric acid at $5-10^{\circ}C$ to form *ortho* and *para* nitro phenols, but the yield is poor due to oxidation of phenolic group. The – OH group is activating group, hence nitration is possible with dilute nitric acid.



It is believed that the mechanism of the above reaction involves the formation of *o*- and *p*- nitroso phenol with nitrous acid, $HNO_2(NaNO_2 + HCl)$ at $O-5^{\circ}C$, which gets oxidised to *o*- and *p*- nitrophenol with dilute nitric acid.



However, when phenol is treated with concentrated HNO_3 in presence of concentrated H_2SO_4 , 2,4,6-trinitrophenol (Picric acid) is formed.



To get better yield $o_{\overline{t}}^{\overline{t}}, 4_{\gamma}$ ficric acid, first sulphonation of phenol is made and then nitrated. Presence of $-SO_{\gamma}H$ group prevents oxidation of phenol.

(d) *Friedel-Craft's reaction* : Phenol when treated with methyl chloride in presence of anhydrous aluminium chloride, *p*-cresol is the main product. A very small@Hount of *o*-cresol is als@Hormed. *OH*



RX and $AlCl_3\,$ give poor yields because $AlCl_3\,$ coordinates with O. So Ring alkylation takes place as follows,

 $C_6H_5OH + AlCl_3 \rightarrow C_6H_5OAlCl_2 + HCl$

Thus to carry out successful Friedel-Craft's reaction with phenol it is necessary to use a large amount of $AlCl_3$. The **Ring alkylation** takes place as follows :



(f) Reimer-Tiemann reaction : Phenol, on refluxing with chloroform and sodium hydroxide (aq.) followed by acid hydrolysis yields salicylaldehyde (o-hydroxy benzaldehyde) and a very small amount of p-hydroxy benzaldehyde. However, when carbon tetrachloride is used, salicylic acid (predominating product) is formed.



(g) *Gattermann's reaction* : Phenol, when treated with liquid hydrogen cyanide and hydrochloric acid gas in presence of anhydrous aluminium chloride yields mainly *p*-hydroxy benzaldehyde (Formylation).

$$HCl + HC \equiv N \xrightarrow{AlCl_3} ClCH = NH$$



(iv) Miscellaneous reactions

(a) *Coupling reactions* : Phenol couples with benzene diazonium chloride in presence of an alkaline solution to form a red dye (p-hydroxy azobenzene).



Phenol couples with phthalic anhydride in presence of concentrated H_2SO_4 to form a dye, (phenolphthalein) used as an indicator.



(b) Condensation with formaldehyde : Phenol condenses with formaldehyde (excess) in presence of sodium hydroxide or acid (H^+) for about a week to form a polymer known as bakelite (a resin).



(c) Liebermann's nitroso reaction : When phenol is reacted with $NaNO_2$ and concentrated H_2SO_4 , it gives a deep green or blue colour which changes to red on dilution with water. When made alkaline with NaOH original green or blue colour is restored. This reaction is known as Liebermann's nitroso reaction and is used as a test of phenol.



(d) *Oxidation* : Phenol turns pink or red or brown on exposure to air and light due to slow oxidation. The colour is probably due to the formation of quinone and phenoquinone.



But on oxidation with potassium persulphate in alkaline solution, phenol forms 1, 4-dihydroxy benzene (Quinol). This is known as Elbs persulphate oxidation.

p



(4) **Uses :** Phenol is extensively used in industry. The important applications of phenol are

(i) As an antiseptic in soaps, lotions and ointments. A powerful antiseptic is "Dettol" which is a phenol derivative (2, 4-dichloro-3, 5-dimethyl phenol).

(ii) In the manufacture of azo dyes, phenolphthalein, etc.

(iii) In the preparation of picric acid used as an explosive and for dyeing silk and wool.

(iv) In the manufacture of cyclohexanol required for the production of nylon and used as a solvent for rubber and lacquers.

(v) As a preservative for ink.

(vi) In the manufacture of phenol-formaldehyde plastics such as bakelite.

(vii) In the manufacture of drugs like aspirin, salol, phenacetin, etc.

(viii) For causterising wounds caused by the bite of mad dogs.

(ix) As a starting material for the manufacture of nylon and artificial tannins.

(x) In the preparation of disinfectants, fungicides and bactericides.

(5) Tests of phenol

(i) Aqueous solution of phenol gives a violet colouration with a drop of ferric chloride.

(ii) Aqueous solution of phenol gives a white precipitate of 2, 4, 6-tribromophenol with bromine water.

(iii) Phenol gives Liebermann's nitroso reaction.

Phenol in conc. sulphuric acid $\xrightarrow{NaNO_2}$ Red colour \xrightarrow{NaOH} Blue colour

(iv) Phenol combines with phthalic anhydride in presence of conc. H_2SO_4 to form phenolphthalein which gives pink colour with alkali, and used as an indicator.

(v) With ammonia and sodium hypochlorite, phenol gives blue colour.

Property	Phenol (C_6H_5OH)	Alcohol (C ₂ H ₅ OH)
Odour	Typical phenolic odour	Pleasant alcoholic odour
Nature, reaction with alkali	Acidic, dissolves in sodium hydroxide forming sodium phenoxide.	Neutral, no reaction with alkalies.
Reaction with neutral <i>FeCl</i> ₃	Gives violet colouration due to formation of complex compound.	No reaction.
Reaction with halogen acids	No reaction with halogen acids.	Forms ethyl halides.
Oxidation	Pink or brown colour due to formation of quinone and phenoquinone.	Undergoes oxidation to give acetaldehyde and acetic acid.
Reaction with <i>HCHO</i>	Forms polymer (bakelite).	No reaction.
Liebermann's nitroso reaction	Positive.	Does not show.
Coupling with benzene diazonium chloride	Forms azo dye.	Does not form any dye.
Reaction with <i>PCl</i> ₅	Mainly forms triphenyl phosphate.	Forms ethyl chloride
Iodoform test	Does not show.	Positive.

Table : 26.2 Difference between phenol and alcohol

Derivatives of phenol







(2) **Properties :** *o*-Nitrophenol is a yellow coloured crystalline compound, while *m*- and *p*-isomers are colourless crystalline compounds.

Isomer	ortho	meta	para
m.pt. (°C)	45	97	114

:

The lowest melting point of *o*-isomer is due to **intramolecular hydrogen bonding** whereas *meta* and *para* isomers possess **intermolecular hydrogen bonding** and thus, they have higher melting points.

They are stronger acids than phenol. The order is

p-isomer > *o*-isomer > *m*-isomer > phenol

When reduced, they form corresponding aminophenols. *o*- and *p*-Nitrophenols react with bromine water to form 2, 4, 6-tribromophenol by replacement of nitro group. *OH*





(1) **Preparation :** It is obtained when phenol is treated with conc. HNO_3 . However, the yield is very poor. It is prepared on an industrial scale :

(i) From chlorobenzene



(ii) From phenol through disulphonic acid





(2) **Properties :** It is a yellow crystalline solid, melting points 122°*C*. it is insoluble in cold water but soluble in hot water and in ether. It is bitter in taste. Due to the presence of three electronegative nitro groups, it is a stronger acid than phenol and its properties are comparable to the carboxylic acid. It neutralises alkalies and decomposes carbonates with evolution of carbon dioxide.

Dry picric acid as well as its potassium or ammonium salts explode violently when detonated. It reacts with PCl_5 to form picryl chloride which on shaking **Or** the NH₃ yields **pi**cramide. NH₂



When distilled with a paste of bleaching powder, it gets decomposed and yields chloropicrin, CCl_3NO_2 , as one of the products and is thus employed for the manufacture of tear gas.

It forms yellow, orange or red coloured molecular compounds called picrates with aromatic hydrocarbons, amines and phenols which are used for characterisation of these compounds.

□ Picrates are explosive in nature and explode violently when heated. These are prepared carefully.



(3) **Uses :** It is used as a yellow dye for silk and wool, as an explosive and as an antiseptic in treatment of burns.

Catechol (1, 2-Dihydroxy benzene)





(2) **Properties :** It is a colourless crystalline solid, melting points $105^{\circ}C$. it is soluble in water. It is affected on exposure to air and light. It acts as a reducing agent as it reduces Tollen's reagent in cold and Fehling's solution on heating. With silver oxide it is oxidised to *o*-benzoquinone.



It forms insoluble lead salt (white ppt.) when treated with lead acetate solution and gives green colour with $FeCl_3$ which changes to red on adding Na_2CO_3 solution. It forms alizarin dye stuff when condensed with phthalic anhydride in the presence of sulphuric acid.



(3) **Uses :** It finds use as photographic developer, in the manufacture of alizarin and adrenaline hormone and as an antioxidant (inhibitor in auto oxidation) for preserving gasoline.

Resorcinol (1, 3-Dihydroxy benzene)

(1) **Preparation :** It is prepared by alkali fusion of 1,3, benzene disulphonic acid (Industrial method).



(2) **Properties :** It is a colourless crystalline solid, melting points 110°*C*. it is affected on exposure by air and light. It is soluble in water, alcohol and ether. It shows tautomerism. Its aqueous solution gives violet colour with $FeCl_3$. It reduces Fehling's solution and Tollen's reagent on warming.

With bromine water, it gives a crystalline precipitate, 2, 4, 6-tribromoresorcinol.



On nitration, it forms 2, 4, 6-trinitro-1, 3dihydroxybenzene.



It condenses with phthalic anhydride and forms



With nitrous acid, it forms 2, 4dinitrosoresorcinol



Resorcinol behaves as a tautomeric compound. This is shown by the fact that it forms a dioxime and a bisulphite derivative. O



(3) **Uses**

(i) It is used as antiseptic and for making dyes.

(ii) It is also used in the treatment of eczema. 2,4, 6-trinitroresorcinol is used as an explosive.

Hydroquinone or quinol (1, 4-Dihydroxy benzene)

(1) **Preparation :** It is formed by reduction of *p*benzoquinone with sulphurous acid $(H_2SO_3) \longrightarrow O+SO_2)$. $O = O+SO_2+2H_2O \rightarrow HO-OH+H_2SO_4$ $H_2SO_3+H_2O$ Quinol

(*p*-Benzoquinone is obtained by oxidation of aniline)



(2) **Properties :** It is a colourless crystalline solid, melting points $170^{\circ}C$. it is soluble in water. It also shows tautomerism. It gives blue colour with $FeCl_3$ solution.

It acts as a powerful reducing agent as it is easily oxidised to *p*-benzoquinone. It reduces Tollen's reagent and Fehling's solution.



Due to this property, it is used as photographic developer.

(3) **Uses :** It is used as an antiseptic, developer in photography, in the preparation of quinhydrone electrode and as an antioxidant.

Trihydric Phenols : Three trihydroxy isomeric derivatives of benzene are **Pyrogallol** (1, 2, 3), hydroxy quinol (1, 2, 4) and phloroglucinol (1, 3, 5).

Pyrogallol is obtained by heating aqueous solution of gallic acid at 220°C.



Phloroglucinol is obtained from trinitrotoluene (TNT) by following sequence of reactions.



Hydroxyquinol is prepared by the alkaline fusion of hydroquinone in air.



The three isomers are colourless crystalline compounds. All are soluble in water and their aqueous solutions give characteristic colour with $FeCl_3$ (Red, brown or bluish violet). Alkaline solutions absorb oxygen rapidly from air.

Uses of pyrogallol

(i) As a developer in photography.

(ii) As a hair dye.

(iii) In treatment of skin diseases like eczema.

(iv) For absorbing unreacted oxygen in gas analysis.

Ether

Ethers are anhydride of alcohols, they may be obtained by elimination of a water molecule from two alcohol molecules.

$$R - OH + HO' - R \rightarrow R - O - R + H_2O$$

General formula is $C_n H_{2n+2} O$

General methods of preparation of ethers

(1) From alkyl halides

(i) Williamson's synthesis

It is a nucleophilic substitution reaction and proceed through $S_{_{N^2}}$ mechanism.

$$RONa + R'X \rightarrow ROR' + NaX$$

$$C_2H_5ONa + CH_3 - I \rightarrow CH_3OC_2H_5 + NaI$$
Sodium ethoxide
Ethyl methylether

$$\begin{array}{c} C_2H_5ONa + C_2H_5Br \rightarrow C_2H_5OC_2H_5 + NaB\\ \text{Sodium ethoxide} \quad \text{Ethyl bromide} \quad \text{Ethoxyethane} \end{array}$$

(a) Order of reactivity of primary halide is $CH_3X > CH_3CH_2X > CH_3CH_2CH_2X$.

(b) Tendency of alkyl halide to undergo elimination is $3^{o} > 2^{o} > 1^{o}$.

(c) For better yield alkyl halide should be primary and alkoxide should be secondary or tertiary.

$$\begin{array}{c} CH_{3} & CH_{3} \\ C_{2}H_{5}Br + NaO - \overset{|}{C} - CH_{3} \rightarrow C_{2}H_{5} - O - \overset{|}{C} - CH_{3} \\ \overset{|}{C} H_{3} & CH_{3} \\ CH_{3} & CH_{3} \\ \overset{|}{C} H_{3} \end{array}$$

(d) Secondary and tertiary alkyl halides readily undergo E_2 elimination in the presence of a strong base to form alkenes.

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

□ Aryl halide and sodium alkoxide cannot be used for preparing phenolic ethers because aryl halide are less reactive toward nucleophilic substitution reaction than alkyl halides.

(ii) By heating alkyl halide with dry silver oxide

$$2RX + Ag_2O \xrightarrow{\text{heat}} R - O - R + 2AgX ,$$

$$2C_2H_5Br + Ag_2O \xrightarrow{\text{heat}} C_2H_5OC_2H_5 + 2AgBr$$

Ethyl bromide Diethyl ether

(2) From alcohols

(i) By dehydration of alcohols

(a) With conc. H₂SO₄ at 140° C

 $\frac{ROH + HOR}{2 \text{ molecules of alcohol}} \xrightarrow[140^{\circ}C]{H_2SO_4(\text{conc.})} ROR + H_2O .$

□ In this reaction alcohol must be present in excess.

□ This reaction is mainly applicable for the dehydration of primary alcohols. Secondary and tertiary alcohols form alkenes mainly.

□ When this reaction is carried out between different alcohols then there is a mixture of different ethers is obtained.

(b) With
$$Al_2O_3$$
 at 250° C:
 $2ROH \xrightarrow{Al_2O_3} R - O - R + H_2O_3$

(ii) By the action of diazomethane on alcohols : This reaction is in presence of catalyst, boron trifluoride or HBF_4 .

$$ROH + CH_2N_2 \xrightarrow{BF_3} R - O - CH_3 + N_2$$

(a) This method is very useful for preparing mixed ethers.

(b) In higher cases, there can be 1, 2-hydride or 1, 2-methyl shift to form more stable carbonium ion.

(3) Alkoxy mercuration-demercuration
>
$$C = C < +R - OH + Hg[OOCCF_3]_2$$

□ This is the best method for the preparation of tethers.

(4) Reaction of lower halogenated ether with grignard reagent

$$\begin{array}{c} ROCH_{2}X + XMgR' \rightarrow ROCH_{2}R' + MgX_{2} \\ \text{Halogenate d} & \text{Grignard} \\ \text{ether} & \text{reagant} & \text{ether} \end{array}$$

(i) Higher members can be prepared by the action of grignard reagent on lower halogenated ethers.

(ii) Ether form soluble coordinated complexes with grignard reagent.

Physical properties

(1) **Physical state :** Methoxy methane and methoxy ethane are gases while other members are volatile liquid with pleasant smell.

(2) **Dipole moment (D.M.) :** Bond angle of ether is due to sp^3 hybridisation of oxygen atom. Since C - O bond is a polar bond, hence ether possess a net dipole moment, even if they are symmetrical. dipole moment of dimethyl ether is 1.3 D and dipole moment of di ethyl ether is 1.18 D.

□ The larger bond angle may be because of greater repulsive interaction between bulkier alkyl groups as compared to smaller H-atoms in water.

(3) **Boiling points :** Boiling points of ethers are much lower than those of isomeric alcohols, but closer to alkanes having comparable mass. This is due to the absence of hydrogen bonding in ethers.

(4) **Solubility :** Solubilities of ethers in water are comparable with those of alcohols.

Example : Di ethyl ether and *n*-butyl alcohol have approximately the same solubility in water. This is because, ether form hydrogen bond with water much in the same way as alcohol do with water.



□ Solubility of ether in water decreases with the size of alkyl groups.

(5) **Hydrogen bonding :** There is no hydrogen directly attach (bonded) to oxygen in ethers, so ethers do not show any intermolecular hydrogen bonding.

(6) **Density :** Ethers are lighter than water.

Chemical properties : Ethers are quite stable compounds. These are not easily attacked by alkalies, dilute mineral acids, active metals, reducing agents or oxidising agents under ordinary conditions.

(1) Reaction due to alkyl group

(i) Halogenation :

$$CH_{3}CH_{2}OCH_{2}CH_{3} \xrightarrow{Cl_{2}} CH_{3}CHClOCH_{2}CH_{3}$$

$$\xrightarrow{dark} CH_{3}CHClOCH_{2}CH_{3} \xrightarrow{(\alpha-Monochloro diethyl ether)} CH_{3}CH_{2}OCH_{2}CH_{3} \xrightarrow{Cl_{2}} CH_{3}CHClOCHClCH_{3}$$

$$\xrightarrow{(\alpha, \alpha'-Dichlorodiethyl ether)} CH_{3}CHClOCHClCH_{3} \xrightarrow{(\alpha, \alpha'-Dichlorodiethyl ether)} CH_{3}CHClOCHClCH_{3} \xrightarrow{(\alpha, \alpha'-Dichlorodiethyl ether)} CH_{3}CHClOCHClCH_{3} \xrightarrow{(\alpha, \alpha'-Dichlorodiethyl ether)} CH_{3}CHCLOCHClCH_{3}CHClOCHClCH_{3} \xrightarrow{(\alpha, \alpha'-Dichlorodiethyl ether)} CH_{3}CHCLOCHCLCH_{3} \xrightarrow{(\alpha, \alpha'-Dichlorodiethyl ether)} CH_{3}CHCLOCHCLCH_{3}$$

 $C_2H_5OC_2H_5 + 10Cl_2 \xrightarrow{Cl_2} C_2Cl_5OC_2Cl_5 + 10HCl$ (ii) **Burning** : Ethers are highly inflammable.

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

(2) Reaction due to ethernal oxygen

(i) Peroxide formation :

They burn like alkanes.

$$C_2H_5 \stackrel{\cdots}{O} C_2H_5 + \stackrel{\cdots}{O} : \rightarrow (C_2H_5)_2 O \rightarrow O.$$

(a) The boiling point of peroxide is higher than that of ether. It is left as residue in the distillation of ether and may cause explosion. Therefore ether may never be evaporated to dryness.

(b) Absolute ether can be prepared by distillation of ordinary ether from conc. H_2SO_4 and subsequent storing over metallic sodium.

 \Box Formation of peroxide can be prevented by adding small amount of Cu_2O to ether.

□ With strong oxidising agent like acid, dichromate ethers are oxidised to aldehydes.

$$CH_3CH_2OCH_2CH_3 \xrightarrow{2[O]} 2CH_3CHO + H_2O$$

Acetaldehyde

□ The presence of peroxide can be indicated by the formation of blood red colour complex in the following reaction.

Peroxide
$$+ Fe^{+2} \rightarrow Fe^{+3} \xrightarrow{SCN^{-}} [Fe(SCN)_n]^{3-n}$$

Blood red colour
 $(n=1 \text{ to } 6)$

(ii) Oxidation with K₂Cr₂O₇ / H[⊕]

$$R - CH_2 - O - CH < R' R'$$

(a) Oxidation of ether can only be possible if any one of the alkyl groups of ether has hydrogen on α -carbon.

(b) α -carbon having two hydrogens converts in carboxylic group and α -carbon having only one hydrogen converts into keto group.

$$CH_{3} - CH_{2} - O - CH_{2} - CH_{2} - CH_{3}$$

$$\xrightarrow{K_{2}Cr_{2}O_{7}}{H^{\oplus}/\Delta} CH_{3} - COOH + CH_{3} - CH_{2} - COOH$$

$$CH_{3} - CH_{2} - O - CH < CH_{3}$$

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

$$\xrightarrow{K_{2}Cr_{2}O_{7}}{H^{\oplus}/\Delta} CH_{3} - COOH + CH_{3} - CH_{3} - CH_{3}$$

(iii) **Salt formation :** Due to lone pair of electrons on oxygen atom. Ether behaves as Lewis base and form stable oxonium salt with strong inorganic acids at low temperature.

$$H$$

$$C_2H_5OC_2H_5 + HCl \rightarrow (C_2H_5)_2 O^+ Cl^- \text{ or }$$
Diethy loxonium chloride

$$[(C_2H_5)_2O\cdot H]^{+}Cl^{+}$$

$$C_2H_5OC_2H_5 + H_2SO_4 \rightarrow (C_2H_5)_2 \stackrel{+}{O}_{+} + HSO_4^{-}$$
 or
 $H_{Diethyloxonium hydrogen sulphate}$

$$[(C_2H_5)_2O \cdot H]^+ HSO_4^-$$

The oxonium salts are soluble in acid solution and ethers can be recovered from the oxonium salts by treatment with water.

$$(C_{2}H_{5})_{2} \underset{H}{O Cl} \xrightarrow{H_{2}O} (C_{2}H_{5})_{2}O + HCl$$

Diethy lether
Diethy lether

□ The formation of oxonium salt is similar to the formation of ammonium salts from ammonia and acids.

 $\hfill\square$ Ether is removed from alkyl halides by shaking with conc. H_2SO_4 .

 $\hfill\square$ Ethers can be distinguished from alkanes with the help of this reaction.

(iv) **Reaction with Lewis acids :** Being Lewis bases, ethers form complexes with Lewis acids such as BF_3 , $AlCl_3$, $FeCl_3$, etc. These complexes are called **etherates**.

$$\begin{array}{c} CH_3CH_2 \\ CH_3CH_2 \end{array} \stackrel{\sim}{\longrightarrow} O : +BF_3 \rightarrow \begin{array}{c} CH_3CH_2 \\ CH_3CH_2 \\ Boron trilloride etherate (complex) \end{array}$$

Similarly, diethyl ether reacts with Grignard reagent forming Grignard reagent etherate.

$$2(CH_{3}CH_{2})_{2}O + RMgX \rightarrow \underset{(CH_{3}CH_{2})_{2}O}{R} \underset{\text{Grignard reasont etherate}}{R} \underset{Mg}{\longrightarrow} \underset{O(CH_{2}CH_{3})_{2}}{\swarrow}$$

Due to the formation of the etherate, Grignard reagents dissolve in ether. That is why Grignard reagents are usually prepared in ethers. However, they cannot be prepared in benzene, because benzene has no lone pair of electrons and therefore, cannot form complexes with them.

(3) Reaction involving cleavage of carbonoxygen bond

(i) Hydrolysis

(a) With dil. H_2SO_4 : $ROR + H_2O \xrightarrow{H_2SO_4} 2ROH$

$$C_2H_5OC_2H_5 + H_2O \xrightarrow{H_2SO_4} 2C_2H_5OH$$

Diethylether Ethanol

(b) With conc. H_2SO_4 :

$$\begin{array}{c} C_2H_5OC_2H_5 + H_2SO_4 \rightarrow C_2H_5OH + C_2H_5HSO_4 \\ C_2H_5OH + H_2SO_4 \rightarrow C_2H_5HSO_4 + H_2O \\ \hline C_2H_5OC_2H_5 + 2H_2SO_4 \rightarrow 2C_2H_5HSO_4 + H_2O \\ \hline \text{Diethy lether} \\ \hline \end{array}$$

(ii) Action of hydroiodic acid

(a) With cold HI

$$C_{2}H_{5}OC_{2}H_{5} + HI \xrightarrow{\text{Cold}} C_{2}H_{5}I + C_{2}H_{5}OH$$

$$\xrightarrow{\text{Diethylether}} HBr \xrightarrow{\text{OH}} + C_{2}H_{5}Br$$
Phenyl ethyl Phenol Ethyl bromidde

(b) With hot HI

$$R - O - R' + 2HI \xrightarrow{\text{heat}} RI + R'I + H_2O$$

(iii) Zeisel method :

 $RI + AgNO_3$ (alc.) $\rightarrow AgI \downarrow + RNO_3$

□ The silver iodide thus form can be detected and estimated. This is the basis of Zeisel method for the detection and estimation of alkoxy group in a compound.

(iv) Action of PCl₅

$$R - O - R + PCl_5 \xrightarrow{\text{heat}} 2RCl + POCl_3$$
. There is

no reaction in cold.

$$CH_{3}COCl + C_{2}H_{5} : O \cdot C_{2}H_{5} \xrightarrow{ZnCl_{2}} CH_{3}COOC_{2}H_{5}$$
Acety khlöride Diethy lether Ethy lacetate

(vi) Reaction with acid anhydride

$$CH_{3}CO \cdot O \cdot OCCH_{3} + C_{2}H_{5} \cdot O \cdot C_{2}H_{5}$$

Acetic anhy dride Diethy lether

 $\xrightarrow{ZnCl_2} 2CH_3COOC_2H_5$ heat Ethylacetate

(vii) Dehydration

$$C_2H_5OC_2H_5 \xrightarrow{Al_2O_3}{300^{\,o}C} 2CH_2 = CH_2 + H_2O$$

(viii) Reaction with carbon mono oxide

$$C_2H_5OC_2H_5 + CO \xrightarrow{BF_3/150^\circ C} C_2H_5COOC_2H_5$$

Diethylether $C_2H_5COOC_2H_5$

(ix) Action of bases

$$\stackrel{+}{Li\overline{C}H_3} \stackrel{-}{+} H \stackrel{-}{-} CH_2 \stackrel{-}{-} CH_2 \stackrel{-}{-} O \stackrel{-}{-} CH_2 - CH_3$$
$$\rightarrow CH_4 + CH_2 = CH_2 + \stackrel{+}{Li\overline{O}C_2}H_5$$

(4) **Ring substitution in aromatic ethers :** Alkoxy group is *ortho* and *para* directing and it directs the incoming groups to *ortho* and *para* position. It activates the aromatic ring towards electrophilic substitution reaction. +OR +OR +OR



III, IV and V show high electron density at *ortho* and *para* position.

(i) **Halogenation :** Phenyl alkyl ethers undergo usual halogenation in benzene ring.

For example, Bromination of anisole gives *ortho* and *para* bromo derivative even in the absence of iron (III) browned catalyst. OCH_3 OCH_3





□ Ethers are relatively less reactive than phenol towards electrophilic substitution reaction.

 \swarrow Methyl alcohol (*CH*₃*OH*) is called wood spirit. It is obtained by destructive distillation of wood. Drinking of methanol causes blindness.

 \mathcal{L} Ethyl alcohol (C_2H_5OH) is called grain alcohol. It is used in preparation of various beverages by using different percentages.

▲ An alcohol-water mixture containing 57.1% alcohol by volume or 49.3% by weight is called proof spirit.

 \mathcal{L} Ethyl alcohol containing 5 to 10% methyl alcohol is called methylated spirit. It is unfit for drinking purpose. Widespread deaths due to liquor poisoning occur mainly due to the presence of methyl alcohol. It is also called denatured spirit. Denaturing can also be done by adding 0.5% pyridine, petroleum naphtha, rubber distillate (caoutchoucine) or *CuSO*₄.

✓ Pyroligneous acid contains acetic acid (10%), methyl alcohol (2.5%) and acetone (0.5%).

E Fusel oil is a mixture of *n*-propyl alcohol, *n*-butyl alcohol, *n*-amyl alcohol and isoamyl alcohol.

 \mathcal{A} Tincture of iodine is 2-3% alcoholic solution of iodine.

✓ In the esterification reaction, the water formed is removed by Dean and stark apparatus. It should be noted that bulkier the acid or alcohol, slower is the rate (due to stearic hinderance). Decreasing order of rate of reaction of different alcohols and acids is
$$\begin{split} CH_3OH > C_2H_5OH > (CH_3)_2CHOH > (CH_3)_3C - OH \\ HCOOH > CH_3COOH > (CH_3)_2CH - COOH > (CH_3)C - COOH. \end{split}$$

✓ Pinacol-pinacolone rearrangement : The reaction involves dehydration of diols through the formation of carbocation intermediate which rearranges to more stable compound.

$$CH_{3} \xrightarrow{I}_{i} CH_{3} \xrightarrow{I}_{i} CH_{3} \xrightarrow{H^{+}}_{-H_{2}O} CH_{3} \xrightarrow{I}_{i} CH_{3} \xrightarrow{H^{+}}_{-H_{2}O} CH_{3} \xrightarrow{I}_{-H_{3}O} CH_{3}$$

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

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

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

✗ In general, acid strength increases as Cresols << Phenol << p-chlorophenol << m-Nitrophenol << o-Nitrophenol << p-Nitrophenol << Picric acid.</p>

✗ Glyceryl trinitrate is an inorganic ester.

∠ Glyceryl trinitrate is colourless, oily liquid insoluble in water and is called Nobel's oil. Nobel's oil is also used in the treatment of anginapectoris and asthma.

 \mathcal{L} Ether peroxide formation is prevented by adding a little Cu_2O to it.

 \mathcal{L} Di-isopropyl ether is used in the petrol as an antiknock compound.

✓ The mixture of alcohol and ether is used as a substitute for petrol under the trade name natelite.

E Ethers form soluble co-ordination complexes with Grignard's reagent *i.e.*, why Grignard reagent is usually prepared in ether.

🙇 Thio alcohols are known as mercaptans.

				Alcohol, Phenol a	nd Ethers 1217
_				(c) (<i>CH</i> ₃) ₂ <i>CHOH</i>	(d) $CH_3CH_2CH(OH)CH_3$
	Ordina	ry Thinking	12.	General formula of prim	nary alcohol is [CPMT 1975]
	G			(a) > <i>CHOH</i>	(b) $\geq C - OH$
		Objective Questions			ОН
				(c) -CH OH	(d) = C
Ger	neral introduction of al	cohol, Phenol & Ethers		$(c) = c n_2 o n$	OH
1.	Butane-2-ol is	[CPMT 1977, 89]	13.	Which of following is pr	nenolic [J & K 2005]
	(a) Primary alcohol	(b) Secondary alcohol		(a) Phthalic acid	(b) Phosphoric acid
	(c) Tertiary alcohol	(d) Aldehyde		(c) Picric acid	(d) Phenylacetic acid
2.	Picric acid is [CP	MT 1971, 80, 81; DPMT 1983;	14.	1, 2, 3-trihydroxybenzer	ie is also known as
		MP PMT 1990; BHU 1996]		(a) Pyrogallol	(b) Phloroglucinol
	(a) Trinitroaniline	(b) Trinitrotoluene		(c) Resorcinol	(d) Quinol
	(c) A volatile liquid	(d) 2, 4, 6 trinitrophenol	1-	Putanal is an ovample of	f [MD DET 1001]
3.	3- pentanol is a	[RPET 2002]	15.		
	(a) Primary alcohol	(b) Secondary alcohol		(a) Primary alcohol	(b) Secondary alcohol
	(c) Tertiary alcohol	(d) None of these		(c) Aliphatic aldehyde	(d) Aliphatic ketone
4.	Glycerol is a		16.	Cyclohexanol is a	
	[DPMT 1984, 200	0; MP PET 2001; J & K 2005]		(a) Primary alcohol	(b) Secondary alcohol
	(a) Primary alcohol	(b) Monohydric alcohol		(c) Tertiary alcohol	(d) Phenol
_	(c) Secondary alconol	(d) Irinyaric alconol	17.	The characteristic grou	ping of secondary alcohols
5.	(a) Hudrowy tolyopog	(b) Dibudric phonols	,	is	
	(a) Hydroxy toluelles	(d) Tribudric alcohole			[DPMT 1984]
6	(c) Thisuic plienois	(u) ITHIYUTIC alcohols		(a) $-CH_{2}OH$	(b) $> CHOH$
0.	(a) Pyrene	(b) Commercine			
	(c) Ethylene glycol	(d) PVC			OH
7.	Ortho-dihydroxy benzer	ne is		(c) $-C - OH$	(d) >C
,.	(a) Carvacrol	(b) Resorcinol			ОН
	(c) Catechol	(d) Orcinol	18.	Which of the following a	are isomers
8.	Glycerine has				[AFMC 2005; BCECE 2005]
	[MP PMT/PET 1988; M	P PMT 1989, 91; AIIMS 1997]		(a) Methyl alcohol and (limethyl ether
	(a) One primary and tw	o secondary <i>–OH</i> groups		(b) Ethyl alcohol and di	methyl ether
	(b) One secondary and t	wo primary <i>–OH</i> groups		(c) Acetone and acetald	enyde
	(c) Three primary – <i>OH</i>	groups		(d) Propionic acid and p	oropanone
	(d) Three secondary $-O$	H groups	19.	The compound HOCH ₂ -	$-CH_2OH$ is
9.	Which of the following i	is tertiary alcohol[DPMT 2000]		(a) Ethane glycol	(b) Ethylene glycol
	$CH_2 - OH$	CH ₂		(c) Ethylidene alcohol	(d) Dimethyl alcohol
	(a) $CH - OH$	(b) $CH_3 - CH_2 - CH_2OH$	20.	Methylated spirit is	
	$CH = OH$			(a) Methanol	(b) Methanol + ethanol
				(c) Methanoic acid	(d) Methanamide
		CH ₃	21.	The structural formula of	of cyclohexanol is[Bihar CEE 1
	CH ₃			CH ₂	CH ₂
	(c) $CH_3 - C - OH$	(d) $CH_3 - CH_2 - OH$		H₂Ç CHOH	H₂Ć CHOH
	 СН			(a)	(b)
10	Which is primary alcoho				
10.	(a) Butane-2-ol	(b) Butane-1-ol		CH_2	CH_2
	(c) Propane-2-ol	(d) Isopropyl alcohol		∕∕СН₂ОН	\sim
11.	Carbinol is	[RPMT 2000]		(c)	(d)
	(a) $C_2 H_5 O H$	(b) <i>CH</i> ₃ <i>OH</i>		\searrow	\searrow

22.	Molecular formula of a	nyl alcohol is		[IIT 1981; CPMT 1989; Bih	ar MEE 1995; MP PET 2001]
	(a) $C_7 H_{14} O$	(b) $C_6 H_{13} O$		(a) <i>n</i> -propylmethyl ethe	r(b) Butan-1- <i>ol</i>
	(c) $C_{z}H_{12}O$	(d) $C_{\varepsilon}H_{10}O$		(c) 2-methylpropan-2-ol	(d) Butanone
~~	Corbolic peid is		36.	Structure of diethyl ethe	er is confirmed by [DPMT 1985]
23.	KCET (Engg./Med.) 190	P PET/PMT 1998; RPET 1999; 99: BHU 2000: MP PET 2003]	aunt	(a) Kolbe's synthesis	(b) Frankland's
	(a) Phenol	(b) Phenyl benzoate	synt	(c) Muntale amthecie	(d) Williamson's
	(c) Phenyl acetate	(d) Salol	svnt	hesis	(d) williamson s
24.	Absolute alcohol is	[RPMT 1997]	37.	Fermentation is an	[CPMT 1977: RPMT 1999]
-	(a) 100% pure ethanol		3/•	(a) Endothermic reactio	n (b)Exothermic reaction
	(b) 95% alcohol + 5% H_2O			(c) Reversible reaction	(d) None of these
	(c) Ethanol + water + phenol		38.	Nitroglycerine is	(,
	(d) 95% ethanol + 5% i	nethanol	0	(a) An ester	(b) An alcohol
25.	Which of the following	is dihydric alcohol[DCE 2004]		(c) A nitro compound	(d) An acid
-5.	(a) Glycerol	(b) Ethylene glycol	39.	Which of the following a	are known as mercaptans
	(c) Catechol	(d) Resorcinol		C C	[Pb. PMT 2002]
26.	Wood spirit is known as	5 [AFMC 2004]		(a) Thio-alcohols	(b) Thio-ethers
	(a) Methanol	(b) Ethanol		(c) Thio-acids	(d) Thio-aldehydes
	(c) Acetone	(d) Benzene			
27.	Oxygen atom in ether is	[MP PMT/PET 1988]		Preparation of alcohol	, Phenol and Ethers
	(a) Very active	(b) Replaceable			
	(c) Comparatively inert	(d) Active	1.	Ethanol is prepared indu	istrially by [MP PMT 1989]
28.	Which of the following	is a simple ether[AFMC 1997]		(a) Hydration of ethylen	e (b)Fermentation of sugars
	(a) CH_3OCH_3	(b) $C_2H_5OCH_3$		(c) Both the above	(d) None of these
	(c) $C_6H_5OCH_3$	(d) $C_6 H_5 O C_2 H_5$	2.	Ethyl alcohol is indu	ustrially prepared from
29.	An example of a com	ound with the functional		ethylene by	[CPMT 1085]
	group '-O-' is	[CPMT 1983]		(a) Permanganate oxida	tion
	(a) Acetic acid	(b) Methyl alcohol		(b) Catalytic reduction	
	(c) Diethyl ether	(d) Acetone		(c) Absorbing in H_2SO_4	followed by hydrolysis
30.	Which of the followin	g do not contain an acyl		(d) Fermentation	
	group		3.	Propene, $CH_3 - CH = CH$	$_2$ can be converted to 1-
	(a) Acid chloride	(b) Amide		propanol by oxidation. W	hich set of reagents among
	(c) Ester	(d) Ether		the following is ideal to e	ffect the conversion[CBSE PMT 199
31.	Name of $(CH_3)_2HC - O - O$	$-CH_2 - CH_2 - CH_3$ is		(a) Alkaline $KMnO_4$	
		[MP PMT 1992]		(b) B_2H_6 and alkaline H_6	H_2O_2
	(a) Isopropyl propyl eth	ner (b) Dipropyl ether		(c) O_3 / Zn dust	
	(c) Di-isopropyl ether	(d) Isopropyl propyl		(d) $OsO_4 / CH_4, Cl_2$	
keto	ne		4.	Which one of the fo	llowing will produce a
32.	Acetals are	[BVP 2003]	1.	primary alcohol by react	ting with CH_3MgI [MP PET 1991]
	(a) Ketones	(b) Diethers		(a) Acetone	(b) Methyl cyanide
	(c) Aldenyde	(d) Hydroxy aldehydes		(c) Ethylene oxide	(d) Ethyl acetate
33.	In ethers, the $C - O - C$	bond angle 1s	5۰	The fermentation of sta	rch to give alcohol occurs
	(a) 180°	(b) 90°		mainly with the help of[CPMT 1971; MH CET 1999; RPMT 20
	(c) 110°	(d) 160°		(a) O_2	(b) Air
34.	According to Lewis concept of acids and bases,			(c) <i>CO</i> ₂	(d) Enzymes
	ether is		6.	Coconut oil upon alkalin	e hydrolysis gives
	(a) Asidia	[CPMT 1994]		[MP PET 1991; AFMC 200	00; KCET 2001; BCECE 2005]
	(a) ACIUIC	(U) Basic		(a) Glycol	(b) Alcohol
25	(c) Neutral	(a) Ampnoteric	_	(c) Glycerol	(a) Ethylene oxide
35.	ether is	s not isomeric with diethyl	7.	into ethanol	glucose and fructose both
				[MP PMT 1989. 90	, 96; CPMT 1983, 84, 86, 94:
				_ 0.0/0-	

	KCET 1989; MNR 1978; MP PET 1994, 99] (a) Diastase (b) Invertase	19.	An organic compound dissolved in dry benzene evolved hydrogen on treatment with sodium. It is
~	(c) Zymase (d) Maltase		[NCERI 1981; SCRA 1990]
8.	Chlorination of toluene in the presence of light		(a) A tertiary amine (d) An alcohol
	Nach gives		(c) A tertiary annue (u) An alconor
	IUT-IFF 1000]		
	(a) α -cresol (b) p -cresol	20.	$A \xrightarrow{K_2 C C_2 O_7} B \xrightarrow{CH_3 Mgl} CH_3 - C - CH_3 . $ The
	(c) 2 4 -dihydroxy toluene (d) Benzyl alcohol		OH
	In the commercial manufacture of ethyl alcohol		reactant A is[MH CET 2002, 03; AFMC 2004; MP PMT/I
•	from starchy substances by fermentation method.		EAMCET 1989; CPMT 1988; MP PET 2000]
	which enzymes stepwise complete the		(a) $CH_3CHOHCH_3$ (b) CH_3COCH_3
	fermentation reaction [BIT 1992]		(c) C_2H_2OH (d) CH_2COOH
	(a) Diastase, maltase and zymase	21	The reaction water $g_{2} = (C_{1} + H_{2}) + H_{2} = (T_{2} + T_{2})$
	(b) Maltase, zymase and invertase	21,	The reaction, water gas $(CO + H_2) + H_2 = 0.5 \text{ K},500$
	(c) Diastase, zymase and lactase		atmosphere in presence of the catalyst Cr_2O_3 / ZnO_1s
	(d) Diastase, invertase and zymase		used for the manufacture of [MP PMT 1989]
о.	Primary alcohols can be obtained from the		(a) HCHO (b) HCOOH
	reaction of the <i>RMgX</i> with [Pb. PMT 2001]		(c) CH_3OH (d) CH_3COOH
	(a) CO_2 (b) HCHO	22	$CH = CH + B H \xrightarrow{NaOH}$ Product
	(c) $CH_{2}CHO$ (d) $H_{2}O$		$H_2 = CH_2 + B_2H_6 + H_2SO_4$
	On heating aqueous solution of henzene		Product in above reaction is
•	diazonium chloride which is formed [CPMT 1088: BHI	I 1080	(a) CH_3CH_2CHO (b) CH_3CH_2OH
	(a) Benzene (b) Chlorobenzene	1900	(c) CH_3CHO (d) None of these
	(c) Phenol (d) Aniline	23.	Phenolphthalein is obtained by heating phthalic
,	Lialth converts acetic acid into	-3.	anhydride with conc. $H_{2}SO_{1}$ and [BHU 1996]
2.			(a) Renzyl alcohol (b) Renzene
	[CPMT 1977; MP PMT 1990, 92]		(a) Benzoi (b) Benzoi cid
	(a) Acetaidenyde (b) Methane	24	Maltose on hydrolysis gives [BHI 1006: CBMT 2001]
	(c) Etnyi alconol (d) Metnyi alconol	24.	(a) Mannose \pm glucose (b) Galactose \pm glucose
3.	Formaldenyde gives an additive product with		(c) Glucose (d) Mannose + fructose
	hydrolysis gives	25.	Absolute alcohol can be obtained from rectified
	[MP PMT/PET 1988]	0	spirit
	(a) Isopropyl alcohol (b) Ethyl alcohol		[KCET 1985]
	(c) Methyl alcohol (d) Propyl alcohol		(a) By removing the water in it using
4.	Benzyl alcohol is obtained from benzaldehyde by		concentrated sulphuric acid
	[CPMT 1983; MNR 1993]		(b) By removing the water using phosphorus
	(a) Fittig's reaction (b) Cannizaro's reaction	pent	oxide
	(c) Kolbe's reaction (d) Wurtz's reaction	1.	(c) By distilling with the appropriate amount of
5۰	Benzene diazonium chloride on boiling with dilute	benz	zene
	sulphuric acid gives[MP PMT 1983]	26	(u) by distilling over plenty of quick lime
	(a) Toluene (b) Benzoic acid	20.	containing which of the following groups (MNR compounds
~	(c) Benzene (d) Phenol		(a) $> C = Q$ (b) $C = N$
6.	The reaction given below is known as		(a) $>C = C$ (b) $=C = N$ (c) $>C = S$ (d) All of these
	$C_2H_5ONa + IC_2H_5 \longrightarrow C_2H_5OC_2H_5 + NaI$		$\langle c \rangle = 0$ (c) fin of these Λ
	[CPMT 1990; KCET 1990; MH CET 2003; Pb. CET 2002]	27.	$Oil + NaOH_{(aq)} \longrightarrow Glycerol + Soap$
	(a) Kolbe's synthesis (b) Wurtz's synthesis		Above reaction is called
	(c) Williamson's synthesis (d)Grignard's synthesis		(a) Saponification (b) Esterification
7.	Salicylaldehyde can be prepared from [CPMT 1983]		(c) Hydrogenation (d) None of these
	(a) Phenol and chloroform	28.	Acetone on treatment with $CH_{-} = Mg = I$ and on
	(b) Phenol, chloroform and sodium hydroxide	_0.	further hydrolycic gives
	(c) Phenol, carbon tetrachloride and NaOH		(a) Isopropyl alcohol (b) Primary alcohol
~	(d) None of these		(a) isopropyr action (b) rillid y diction (c) Acetic acid (d) 2-methyl 2-propagal
5.	If formaldenyde and potassium hydroxide are	20	(c) Accure actu (u) 2-methyl 2-propanor In the following reaction '4' is
	(a) Acetylono (b) Methane	29.	in the following reaction A 15
	(a) Activitie (D) Methane (c) Methyl alcohol (d) Ethyl formata		
	(c) methyr aconor (d) Ethyr formate		

			Alcohol, Phenor and Ethers 1221
	[BVP 2003]	59.	$C_6H_5 - CH = CHCHO \xrightarrow{X} C_6H_5CH = CHCH_2OH$. In
	(a) Dehydration reaction		the above sequence <i>X</i> can be [DCE 2004]
	(c) Hydrogenation reaction		(a) H_2 / Ni (b) $NaBH_4$
	(d) Heterolytic fission reaction		(c) $K Cr O / H^+$ (d) Both (a) and (b)
50.	The compound formed when ethyl bromide is	6	(c) $K_2 C_2 C_7 / H$ (d) both (d) and (b)
	heated with dry silver oxide is [MP PET/PMT 1988]		Alkenes convert into alcohols by [MP PET 1991]
	(a) Dimethyl ether (b) Diethyl ether		(a) Hydrolysis by dil. H_2SO_4
51	(c) Methyl alconol (d) Ethyl alconol The reagent used for the preparation of higher		(b) Hydration of alkene by alkaline $KMnO_4$
51.	ether from halogenated ethers is[Tamil Nadu CET 2001	L]	(c) Hydrolysis by water vapours and conc. H_2SO_4
	(a) conc. H_2SO_4 (b) Sodium alkoxide		(d) Hydration of alkene by aqueous KOH
	(c) Dry silver oxide (d) Grignard reagent	61.	Acetic acid and CH_3OH are obtained on large
52.	Acetyl bromide reacts with excess of CH_3MgI		scale by destructive distillation of
	followed by treatment with a saturated solution		(a) Wood (b) Coal
	of NH_4Cl gives		(c) Turpentine (d) Crude oil
	[AIEEE 2004] (a) 2-methyl-2-propanol (b) Acetamide	62.	Which is formed when benzalamine react with
	(c) Acetone (d) Acetyl iodide		nitrous acid
53.	What is obtained when chlorine is passed in		[KCET (Med.) 2001]
	boiling toluene and product is hydrolysed[DCE 2004]		(a) $C_6 H_5 OH$ (b) $C_6 H_5 ON$
	(a) <i>o</i> -Cresol (b) <i>p</i> -Cresol		(c) $C_2H_5N_2OH$ (d) $C_6H_5CH_2OH$
54	(c) 2, 4-Dinydroxytoluene (d) Benzyl alcohol Which of the following is formed when	63.	Acid catalyzed hydration of alkenes except ethene
54.	benzaldehyde reacts with sodium hydroxide[Pb. CET 2	2002]	leads to the formation of [AIEEE 2005]
	(a) Benzyl alcohol (b) Benzoic acid		(a) Primary alcohol
	(c) Glucose (d) Acetic acid		(b) Secondary or tertiary alcohol
55.	When ethanal reacts with CH_3MgBr and		(c) Mixture of primary and secondary alcohols
	C_2H_5OH /dry HCl the product formed are[DCE 2003]		(d) Mixture of secondary and tertiary alcohols
	(a) Ethyl alcohol and 2-propanol	64.	Methylphenyl ether can be obtained by reacting
	(b) Ethane and hemi-acetal		[J & K 2005]
	(c) 2-propanol and acetal		(a) Phenolate ions and methyl iodide
	(d) Propane and methyl acetate		(b) Methoxide ions and bromobenzene
56.	Which of the following is industrially prepared by		(c) Methanol and phenol
	passing ethylene into hypochlorous acid[BHU 2004]		(d) Bromo benzene and methyl bromide
	(a) Ethylene glycol (b) Ethylene oxide		
	(c) Ethylene dinitrate (d) Ethane	_	Properties of alcohol, Phenol and Ethers
57.	In which case methyl- <i>t</i> -butyl ether is formed		
	[Orissa JEE 2004]	1.	Which compound is formed when CH_3OH reacts
	(a) $(C_2H_5)_3CONa + CH_3Cl$		with $CH_3 - Mg - X$ [CPMT 1977, 89]
	(b) $(CH_3)_3 CONa + CH_3Cl$		(a) Acetone (b) Alcohol
	(c) $(CH_3)_3 CONa + C_3H_5Cl$		(c) Methane (d) Ethane
	(d) (CH_{-}) , $CON_{a} + CH_{-}Cl$	2.	A compound X of formula C_0H_0O vields a
-0	(a) (ch _{3/3} conu - ch ₃ cu		compound $C_2H_{\epsilon}O$, on oxidation. To which of the
58.	which of the following combinations can be used		following classes of compounds could X being Db Di
	(a) CH MoL and CH COCH		(a) Secondary alcohol (b) Alkene
	(a) CH_3 ing CH_3 $CUCH_3$		(c) Aldehyde (d) Tertiary alcohol
	(b) CH_3MgI and C_2H_5OH	2	The boiling point of alcohol are then
	(c) CH_3MgI and $CH_3COOC_2H_5$	ۍ.	corresponding thiols [Pb. PMT 2000]
	(d) CH_3MgI and $HCOOC_2H_5$		(a) More (b) Same
			(0) 54416

(c) Either of these (d) Less

Methyl alcohol can be distinguished from ethyl 4. alcohol using

[KCET 1984; BHU 2000]

- (a) Fehling solution
- (b) Schiff's reagent
- (c) Sodium hydroxide and iodine
- (d) Phthalein fusion test
- A compound X with molecular formula C_3H_8O can 5٠ be oxidised to a compound Y with the molecular formula $C_3H_6O_2$ X is most likely to be[MP PMT 1991]

(a) Primary alcohol	(b) Secondary alcohol
(c) Aldehyde	(d) Ketone

- 6. An alcohol on oxidation is found to give CH_3COOH and CH_3CH_2COOH . The structure of the alcohol is [BIT 1990]
 - (a) $CH_3CH_2CH_2OH$
 - (b) $(CH_3)_2 C(OH)CH_2 CH_3$
 - (c) $CH_3CH_2CHOHCH_3$
 - (d) $CH_3CH(OH)CH_2CH_2CH_3$
- An organic liquid A containing C, H and O has a 7. pleasant odour with a boiling point of $78^{\circ}C$ On boiling A with conc. H_2SO_4 a colourless gas is produced which decolourises bromine water and alkaline $KMnO_4$. One mole of this gas also takes one mole of H_2 . The organic liquid A is

[KCET 1993]

(a) C_2H_5Cl (b) C_2H_5CHO

(d) C_2H_5OH (c) $C_2 H_6$

- An aromatic amine (A) was treated with alcoholic 8. potash and another compound (Y) when foul smelling gas was formed with formula C_6H_5NC . Y was formed by reacting a compound (Z) with Cl_2 in the presence of slaked lime. The compound (Z) is [CBSE PMT 1990]
 - (a) $C_6H_5NH_2$ (b) C_2H_5OH
 - (c) CH_3OCH_3 (d) $CHCl_3$
- Rectified spirit obtained by fermentation contains 9. 4.5% of water. So in order to remove it, rectified spirit is mixed with suitable quantity of benzene and heated. Benzene helps because [KCET 1987] (a) It is dehydrating agent and so removes water
 - (b) It forms the lower layer which retains all the water so that alcohol can be distilled off
 - (c) It forms an azeotropic mixture having high boiling point and thus allows the alcohol to distill over
 - (d) It forms low boiling azeotropic mixtures which distill over, leaving behind pure alcohol which can then be distilled

- **10.** $C_6H_5OH + ClCOCH_3 \xrightarrow{\text{aq. NaOH}} C_6H_5OCOCH_3$
 - is an example of
 - (a) Dow's reaction
 - (b) Reimer-Tiemann reaction
 - (c) Schotten-Baumann reaction
 - (d) Kolbe's reaction
- Ortho-nitrophenol is steam volatile whereas para-11.
 - nitrophenol is not. This is due to [CBSE PMT 1989] (a) Intramolecular hydrogen bonding present in ortho-nitrophenol
 - (b) Intermolecular hydrogen bonding
 - (c) Intramolecular hydrogen bonding present in para-nitrophenol
 - (d) None of these
- 12. Reaction of phenol with dil. HNO3 gives

[BHU 1984]

(c) Picric acid (d)
$$o$$
- and m -

nitrophenols

- **13.** Phenol is less acidic than
 - [IIT-JEE 1986; UPSEAT 2003; Orissa JEE 2004]
 - (a) Acetic acid (b) *p*-nitrophenol
 - (c) Both (a) and (b) (d) None of these
- The strongest acid among the following aromatic 14. [NCERT 1978] compounds is (a) *ortho*-nitrophenol (b) para-chlorophenol
 - (c) *para*-nitrophenol (d) meta-nitrophenol
- Diazo-coupling is useful to prepare some 15.

[CBSE PMT 1994]

- (a) Pesticides (b) Proteins
- (c) Dyes (d) Vitamins
- 16. Glycerol reacts with $P_4 + I_2$ to form[CBSE PMT 1991] (a) Aldehyde (b) Allyl iodide
 - (c) Allyl alcohol (d) Acetylene
- When glycerine is added to a litre of water which 17.
- of the following behaviour is observed[NCERT 1977; BHU 19 (a) Water evaporates more easily
 - (b) The temperature of water is increased
 - (c) The freezing point of water is lowered
 - (d) The viscosity of water is lowered
- 18. Final product formed on reduction of glycerol by hydroiodic acid is [CPMT 1987] (a) Propane (b) Propanoic acid (c) Propene (d) Propyne
- Glycerol was distilled with oxalic acid crystals 19. and the products were led into Fehling solution and warmed. Cuprous oxide was precipitated. It is [KCET 1987] due to (a) CO (b) HCHO (c) CH_3CHO (d) HCOOH
- Kolbe-Schmidt reaction is used for [CBSE PMT 1991] 20. (a) Salicylic acid (b) Salicylaldehyde
 - (d) Hydrocarbon
- Which of the following explains the viscous 21. nature of glycerol [JIPMER 1997] (b) Hydrogen bonds (a) Covalent bonds
 - (c) Vander Wall's forces (d) Ionic forces

(c) Phenol

22.	On heating glycerol with conc. H_2SO_4 , a	32.	Reaction : $CH_3OH + O_2 -$	$\xrightarrow{600^{0}C}$ product
	compound is obtained which has a bad odour. The		The was deat is	
	COMPOUND IS		The product is	[RPET 2000]
	(a) Glycerol sulphate (b) Acrolein		(a) $CH_2 = C = O$	(b) $H_2 C = O$
	(c) Formic acid (d) Allyl alcohol		(c) $C_2 H_4$	(d) $C_2 H_2$
23.	Isopropyl alcohol on oxidation forms [CPMT 1971, 81, 94; RPMT 2002]	33.	Ethylene glycol, on oxid gives	lation with per-iodic acid,
	(a) Acetone (b) Ether (c) Ethylone (d) Acetaldebyde			[NCERT 1983; CPMT 1983]
24.	Benzenediazonium chloride on reaction with		(a) Oxalic acid	(b) Glycol
-7.	phenol in weakly basic medium gives[IIT-JEE 1998]		(c) Formaldehyde	(d) Glycollic acid
	(a) Diphenyl ether (b) <i>p</i> -	34.	An unknown compoun	d 'D', first oxidised to
hydr	oxyazobenzene		aldehyde and then acitie	c acid by a dilute solution
25	(c) Chlorobenzene (d) Benzene		of $K_2 Cr_2 O_7$ and $H_2 SO_4$. T	he unknown compound 'D'
25.	with $Z_nCl_n + conc_HCl$ at room temperature		is	[BHU 2000]
	[EAMCET 1997; MP PMT 1989, 99; IIT JEE 1981, 86;		(a) CH ₃ CHO	(b) CH_2CH_3OH
	CBSE PMT 1989; CPMT 1989; MP PET 1997; [IPMER 1999]		(c) CH_3CH_2OH	(d) $CH_3CH_2CH_3$
	(a) 1-hydroxybutane	35.	The reaction of ethylene	glycol with PI_3 gives
	(b) 2-hydroxybutane			[MP PMT 2000]
	(c) 2-nydroxy-2-metnylpropane (d) 1-bydroxy-2-methylpropane		(a) ICH_2CH_2I	(b) $CH_2 = CH_2$
26.	The reagent which easily reacts with ethanol and		(c) $CH_{a} = CHI$	(d) $ICH = CHI$
	propanol is	26	The compound (A) w	then treated with some
	[MP PET 1989](a) Fehling solution(b) Grignard reagent(c) Schiff's reagent(d) Tollen's reagent	36.	ammonium nitrate solut compound ' <i>A</i> ' is	tion gives yellow ppt. The
27.	Propene is the product obtained by			[MP PET 2002]
	dehydrogenation of		(a) Alcohol	(b) Aldehyde
	(a) 2-propanol (b) 1-propanol		(c) Acid	(d) Alkane
	(c) Propanal (d) <i>n</i> -propyl alcohol	37.	Which of the following	product is formed, when
28.	Which of the following statements is correct [BHU 199	97]	ether is exposed to air	[AIIMS 2000; RPMT 2002]
	(a) Phenol is less acidic than ethyl alcohol		(a) Oxide	(b) Alkanes
	(c) Phenol is more acidic than carboxylic acid		(c) Alkenes	(d) Peroxide of diethyl
	(d) Phenol is more acidic than carbonic acid		ether	
29.	Boiling point of alcohol is comparatively higher than that corresponding alkane due to[MH CET 2002]	38.	During dehydration of heating with conc. H_2SO	alcohols to alkenes by 4 the initiation step is[AIEEE 200]
	(a) Intermolecular hydrogen bonding		(a) Protonation of alcoh	ol molecule
	(b) Intramolecular hydrogen bonding	(b) Formation of carboc	ation	
	(c) Volatile nature (d) None of these		(c) Elimination of water	•
30.	When Phenol is heated with phthalic anhydride in		(d) Formation of an este	er
0	concentrated sulphuric acid and the hot reaction	39.	Phenol is less acidic that	[MNR 1995]
	mixture is poured into a dilute solution of sodium		(a) Ethanol	(b) Methanol
	hydroxide, the product formed is[MP PET 1997, 2003; F	RPMT :	1999; (c) o-nitrophenol	(d) p -methylphenol
	(a) Alizarin (b) Methyl orange	40.	The compound which	gives the most stable
	(c) Fluorescein (d) Phenolphthalein	70.	carbonium on dehvdrati	on is [MNR 1995]
31.	$CH_3 - CH = CH - CH(OH) - CH_3 \xrightarrow{\text{Jon's}} X,$		(a) $CH_3 - CH - CH_2OH$	
	Product X is [RPET 2000]			
	(a) $CH_3CH_2CH_2CH(OH)CH_3$			
	(b) $CH_3CH = CHCOCH_3$			
	(c) Both (a) and (b) are correct			

(d) $CH_3CH_2CH_2COCH_3$

$$CH_{3}$$

$$|$$
(b) $CH_{3} - C - OH$

$$|$$

$$CH_{3}$$
(c) $CH_{3} - CH_{2} - CH_{2} - CH_{2}OH$
(d) $CH_{3} - CH - CH_{2} - CH_{3}$

$$OH$$

41. At higher temperature, iodoform reaction is given by

		[AIIMS 2003]
	(a) $CH_3CO_2CH_3$	(b) $CH_3CO_2C_2H_5$
	(c) $C_6H_5CO_2CH_3$	(d) $CH_3CO_2C_6H_5$
42.	Cresol has	[CPMT 2003]
	(a) Alcoholic – <i>OH</i>	(b) Phenolic – <i>OH</i>
	(c) - <i>COOH</i>	(d) - <i>CHO</i>
43 .	In $CH_3CH_2OH \xrightarrow{X} CH_2$	$_{2}=CH_{2}+H_{2}O;$
	'X' is	

(c) P₂O₅
(d) Al₂O₃
44. Sodium phenoxide reacts with CO₂ at 400 K and 4-7 atm pressure to give [MP PET 1996]
(a) Sodium salicylate
(b) Salicylaldehyde
(c) Catechol
(d) Benzoic acid

(b) $CaCl_2$

45. The reaction of C_2H_5OH with H_2SO_4 does not give

-	[]	MP PET 1996]
(a) Ethylene	(b) Diethyl e	ther
(c) Acetylene	(d) Ethyl	hydrogen

sulphate

(a) NaCl

- 46. The order of stability of carbonium ions is [MP PET 1996]³.
 - (a) Methyl > ethyl > iso-propyl > tert-butyl
 - (b) Tert-butyl > iso-propyl > ethyl > methyl
 - (c) Iso-propyl > tert-butyl > ethyl > methyl
 - (d) Tert-butyl > ethyl > iso-propyl > methyl

47. Which statement is not correct about alcohol[AFMC 199ta]ste

- (a) Alcohol is lighter than water
- (b) Alcohol evaporates quickly
- (c) Alcohol of less no. of carbon atoms is less soluble in water than alcohol of high no. of carbon atoms
- (d) All of these
- **48.** An organic compound A reacts with sodium metal and forms B. On heating with conc. H_2SO_4 , A gives diethyl ether. A and B are **[AFMC 1998]**
 - (a) C_2H_5OH and C_2H_5ONa (b) C_3H_7OH and CH_3ONa
 - (c) CH_3OH and CH_3ONa

(d) $C_4 H_9 OH$ and $C_4 H_9 ONa$ In the Liebermann's nitroso reaction, sequential 49. changes in the colour of phenol occurs as [AFMC 1998; BHU 1999] (a) Brown or red \rightarrow green \rightarrow red \rightarrow deep blue (b) Red \rightarrow deep blue \rightarrow green (c) Red \rightarrow green \rightarrow white (d) White \rightarrow red \rightarrow green Which one of the following reactions does not 50. yield an alkyl halide [EAMCET 1998] (a) Diethyl ether $+Cl_2$ (b) Diethyl ether +HI(c) Diethyl ether and PCl_5 (d) Diethyl ether $\xrightarrow{\text{Reduction}} X \xrightarrow{SO_2Cl_2} \longrightarrow$ Compound A reacts with PCl_5 to give B which on 51. treatment with KCN followed by hydrolysis gave propionic acid. What is A and B respectively[EAMCET 1998 (a) C_3H_8 and C_3H_7Cl (b) C_2H_6 and C_2H_5Cl (c) C_2H_5Cl and C_2H_5Cl (d) C_2H_5OH and C_2H_5Cl The increasing order of acidity among phenol, p-52. methylphenol, *m*-nitrophenol and *p*-nitrophenol is [CBSE PMT 1995; RPMT 2002] (a) *m*-nitrophenol, *p*-nitrophenol, *p*henol, *p*methylphenol (b) p-methylphenol, m-nitrophenol, phenol, pnitrophenol (c) p-methylphenol, phenol, m-nitrophenol, pnitrophenol (d) Phenol, p-methylphenol, p-nitrophenol, mnitrophenol Which of the following is not characteristic of alcohols [AFMC 1992] (a) Lower alcohols are stronger and have bitter taste (b) Higher alcohols are stronger and have bitter (c) The boiling points of alcohols increase with increasing molecular mass (d) The lower alcohols are soluble in water 54. In reaction of alcohols with alkali metal, acid etc.

- which of the following alcohol will react fastest[BHU 1984
 - (a) Secondary (b) Tertiary

metal is

- (c) Primary (d) All equal55. Order of reactivity of alcohols towards sodium

[Pb. CET 1985]

- (a) Pri > Sec > Ter (b) Pri > Sec < Ter
- (c) Pri < Sec > Ter (d) Pri < Sec < Ter
- **56.** 23 *g* of *Na* will react with methyl alcohol to give

[NCERT 1972] (a) One mole of oxygen (b) One mole of H_2

(c) $\frac{1}{2}$ mole of H_2 (d) None of these

57. Which reagent is useful in converting 1-butanol to 1-bromobutane [EAMCET 1989]
(a) CHBr₃
(b) Br₂

(c) CH_3Br (d) PBr_3

58. The -OH group of methyl alcohol cannot be replaced by chlorine by the action of [KCET 1989] (a) Chlorine

(b) Hydrogen chloride

- (c) Phosphorus trichloride
- (d) Phosphorus pentachloride

59. Which of the following gives ketone on oxidation



60. Phenol is treated with bromine water and shaken well. The white precipitate formed during the process is

[KCET (Med.) 2001; BIT 1992; AIIMS 1996; KCET 2001] (a) *m*-bromophenol

(b) 2, 4-dibromophenol

(c) 2, 4, 6-tribromophenol

(d) A mixture of o- and p-bromophenols

61. Which compound has the highest boiling point **[MP PET 2003]**

(a) Acetone	(b) Diethyl ether
(c) Methanol	(d) Ethanol

- 62. When vapour of ethanol are passed over platinised asbestos in excess of air, the compound formed is [CPMT 1983]
 (a) CH₃CHO
 (b) CH₃COCH₃
 - (c) C_2H_2 (d) CH_3COOH
- 63. Dehydration of ethanol gives [CPMT 1985; BHU 1989]
 - (a) Acetic acid (b) Ethane
 - (c) Ethylene (d) Acetylene
- 64. Which of the following compound will give positive iodoform test [MP PMT 1986, 99; SCRA 1991; CPMT 1994]

(a)
$$CH_3OH$$
 (b) CH_3-C

$$CH_3$$

 $-C - OH$ (d) $CH CH CH CH$

(c)
$$CH_3 - C - OH$$
 (d) $CH_3 CH_2 CH_2 OH$

65. Absolute ethanol cannot be obtained by simple fraction of a solution of ethanol and water because

[KCET 1984; MP PMT 1987]

н

-OH

(a) Their B.P.'s are very nearer

- (b) Ethanol remains dissolved in water
- (c) They form a constant boiling mixture
- (d) Ethanol molecules are solvated
- 66. The alcohol which easily reacts with conc. *HCl* is [MP PMT 1985]
 - (a) $CH_3 CHOH CH_2 CH_3$
 - (b) $(CH_3)_3 C OH$

(c)
$$CH_3 - CH_2 - CH_2 - CH_2 - OH$$

- (d) $(CH_3)_3 CH CH_2OH$
- **67.** In the following series of chemical reactions, identify *Z*

$$C_3H_7OH \xrightarrow{Conc.H_2SO_4} X \xrightarrow{Br_2} Y \xrightarrow{Excess of} Z$$

160–180°C

(a)
$$CH_3 - CH - CH_2$$

 $NH_2 NH_2$
(b) $CH_3 - CH - CH_2$
 OH
(c) $CH_3 - C = CH_2$
 OH
(d) $CH_3C \equiv CH$

- 68. Alcohols of low molecular weight are[CPMT 1976, 89; Pb. PMT 2000]
 - (a) Soluble in water
 - (b) Soluble in all solvents
 - (c) Insoluble in all solvents
 - (d) Soluble in water on heating
- 69. Which of the following compounds is oxidised to prepare methyl ethyl ketone [DCE 2001]
 (a) 2 propanol
 (b) 1 butanol
 (c) 2 butanol
 (d) Tert-butyl alcohol
- **70.** Which of the following is acidic

[CBSE PMT 2001; MH CET 2001]

- (a) CH_3OH (b) C_6H_5OH
- (c) $(CH_3)_2 CHOH$ (d) $CH_3 CH_2 OH$
- 71. With excess bromine, phenol reacts of form[BHU 2001]



(d) Mixture of (a) and (b)

72. Which is obtained on treating phenol, with dilute HNO_3



(c)
$$O_2N \xrightarrow{OH} NO_2$$
 (d) None of these

- 73. Primary alcohols on dehydration give [NCERT 1986]
 (a) Alkenes
 (b) Alkanes
 - (c) Both (a) and (b) (d) None of these
- 74. Primary and secondary alcohols on action of reduced copper give [CPMT 1982; MP PMT 1985;
 EAMCET 1987, 93; MP PET 1995]
 - (a) Aldehydes and ketones respectively
 - (b) Ketones and aldehydes respectively
 - (c) Only aldehydes

NO₂

- (d) Only ketones
- **75.** Methyl alcohol on oxidation with acidified $K_2Cr_2O_7$ gives

[MNR 1987]

[RPMT 1999]

- (a) CH_3COCH_3 (b) CH_3CHO (c) HCOOH(d) CH_3COOH
- **76.** Ethyl alcohol on oxidation with $K_2Cr_2O_7$ gives
 - [MNR 1987; Bihar CEE 1995; UPSEAT 2000]
 - (a) Acetic acid(b) Acetaldehyde(c) Formaldehyde(d) Formic acid
 - (c) Formaldehyde (d) Formic Lucas test is used for
- **77.** Lucas test is used for
 - [CBSE PMT 1990; AIIMS 2002; AFMC 2005] (a) Alcohols (b) Amines
 - (c) Diethyl ether (d) Glacial acetic acid
- **78.** When phenol reacts with ammonia in presence of
 $ZnCl_2$ at 300°C, it gives [AFMC 2001]
 - (a) Primary amine(b) Secondary amine(c) Tertiary amine(d) Both (b) and (c)
- **79.** Azo-dyes are prepared from **[CPMT 2001]**
 - (a) Aniline (b) Benzaldehye
 - (c) Benzoic acid (d) Phenol
- **80.** A compound that easily undergoes bromination is [KCET (Engg.) 2002]
 - (a) Phenol (b) Toluene
 - (c) Benzene (d) Benzoic acid
- 81. Which of the following has lowest boiling point [MH CET 1999](a) *p*-nitrophenol(b) *m*-nitrophenol
 - (c) o-nitrophenol (d) phenol
- **82.** In esterification, the reactivity of alcohols is[**DPMT 2000**]
 - (a) $1^{\circ} > 2^{\circ} > 3^{\circ}$ (b) $3^{\circ} > 2^{\circ} > 1^{\circ}$
 - (c) Same in all cases (d) None of these
- **83.** The role of conc. H_2SO_4 in the esterification process is
 - (a) Catalyst
 - (b) Dehydrating agent

- (c) Hydrolysing agent
- (d) Dehydrating agent and catalyst
- 84. Methanol and ethanol are distinguished by the[MP PET 1999]
 - (a) Action of *HCl* (b) Iodoform test
 - (c) Solubility in water (d) Sodium
- **85.** For phenol, which of the following statements is correct

[MP PMT 1995]

- (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
- **86.** The reaction of Lucas reagent is fast with [MP PMT 2000] (a) $(CH_3)_2 COH$ (b) $(CH_3)_2 CHOH$
 - (c) $CH_3(CH_2)_2OH$ (d) CH_3CH_2OH
- 87. Which of the following reagents convert the propene to 1-propanol [CBSE PMT 2000]
 (a) H₂O, H₂SO₄
 - (b) Aqueous *KOH*
 - (c) $MgSO_4$, $NaBH_4/H_2O$
 - (d) B_2H_6, H_2O_2, OH^-
- 88. Compound 'A' reacts with PCl₅ to give 'B' which on treatment with KCN followed by hydrolysis gave propanoic acid as the product. What is 'A'[CBSE PMT (a) Ethane
 (b) Propane
 - (c) Ethyl chloride (d) Ethyl alcohol
- **89.** Which reagent can convert acetic acid into ethanol
- [BVP 2003]
 (a) Na + alcohol
 (b) LiAlH₄ + ether
 (c) H₂ + Pt
 (d) Sn + HCl
 90. Which of the following would undergo dehydration most readily [UPSEAT 2000]
 (a) 1-phenyl-1butanol
 (b) 2-phenyl-2-butanol
 (c) 1-phenyl-2-butanol
 (d) 2-phenyl-1-butanol
 91. Phenol and benzoic acid is distinguished by[BHU 2003]
 - (a) NaOH (b) $NaHCO_3$
 - (c) Na_2CO_3 (d) H_2SO_4
- **92.** Electrophilic substitution reaction in phenol take place at

[RPMT 2002]

(a) p- position
(b) m- position
(c) o- position
(d) o- and p- position
93. Liebermann's test is answered by [KCET 1998]

Alcohol, Phenol and Ethers 1227 (a) Aniline (b) Methylamine (a) A white crystalline solid (b)A transparent liquid (d) Phenol (c) A gas (d) Yellow solution (c) Ethyl benzoate 94. In the sequence of the following reactions [MP PMT 200294. At low temperature phenol reacts with Br_2 in CS_2 $CH_3CH_2OH \xrightarrow{[0]} X \xrightarrow{[0]} ChromicAcid ChromicAcid CH_3COOH$ to form [MP PET 1991; CPMT 1981; MP PMT 1990; X is IIT 1982; RPMT 2000] (b) *CH*₃*CHO* (a) CH_3COCH_3 (a) *m*-bromophenol (b) o-and p-bromophenol (c) *p*-bromophenol (d) 2, 6-4, (c) CH_3OCH_3 (d) CH_3CH_2COOH tribromophenol The boiling point of glycerol is more than 95. 105. Oxidation of ethanol by chromic acid forms [MP PET 1992] propanol because of [CPMT 1997, 2002] (a) Ethanol (b) Methanol (a) Hydrogen bonding (b) Hybridisation (c) 2-propanone (d) Ethanoic acid (c) Resonance (d) All the above 106. Which of the following not gives effervescence 96. Which of the following produces violet colour with NaHCO₃ [MP PET 1992] with FeCl₃ solution (a) Phenol (b) Benzoic acid (a) Enols (b) Ethanol (c) 2, 4-dinitrophenol (d) 2, 4, 6-trinitrophenol (c) Ethanal (d) Alkyl halides **107.** Conc. H_2SO_4 reacts with C_2H_5OH at $170^{\circ}C$ to **97.** When heated with NH_3 under pressure alone or form in presence of zinc chloride phenols are converted [MP PMT 1991; MP PET 1991; IIT-JEE 1981; into EAMCET 1979; KCET 2001] [RPMT 1997] (a) CH_3COCH_3 (b) CH₃COOH (a) Aminophenols (b) Aniline (c) CH_3CHO (d) $C_{2}H_{4}$ (c) Nitrobenzene (d) Phenyl 108. Which compound has hydrogen bonding hydroxylamine [MP PMT 1992; MP PET 1991] Because of resonance the oxygen atom of -OH98. (a) Toluene (b) Phenol group of phenol (c) Chlorobenzene (d) Nitrobenzene (a) Acquires positive charge (b)Acquires negative charge **109.** Which statement is true [MP PMT 1991] (c) Remains uneffected (d) Liberates (a) C_6H_5OH is more acidic than C_2H_5OH 99. When glycerol is heated with $KHSO_4$ it gives (b) C_6H_5OH is less acidic than C_2H_5OH [CPMT 1974, 85; MP PMT 1988, 90, 91, 92, 94; (c) C_6H_5OH react with NaHCO₃ MP PET 1988, 92] (a) $CH_2 = CH - CH_3$ (b) $CH_2 = CH - CH_2OH$ (d) C_6H_5OH gives oxime with NH_2OH and HCl(c) $CH_2 = CH - CHO$ (d) $CH_2 = C = CH_2$ **110.** Read the following statements carefully : **100.** An organic compound *X* on treatment with (A) A secondary alcohol on oxidation gives a acidified $K_2 Cr_2 O_7$ gives a compound Y which ketone reacts with I_2 and sodium carbonate to form tri-(B) Ethanol reacts with conc. H_2SO_4 at 180 ° C to odomethane. The compound X is [KCET 1996] yield ethylene (a) CH_3OH (b) $CH_3 - CO - CH_3$ (C) Methanol reacts with iodine and sodium hydroxide to give a yellow precipitate of (c) CH_3CHO (d) $CH_3CH(OH)CH_3$ iodoform **101.** The reaction of conc. HNO_3 and phenol forms (D) Hydrogen gas is liberated when sodium is [MP PMT/PET 1988; BHU 1988; MP PMT 1999; Pb. PMT 2000] added to alcohol. Select the correct statements (a) Benzoic acid (b) Salicylic acid from the above set: (c) o-and p-nitrophenol (d) Picric acid (a) A, B (b) C, D 102. Phenol is [MP PMT 1990; UPSEAT 1999] (c) A, B, D (d) A, C, D (a) A weaker base than NH_3 **111.** The following reaction : (b) Stronger than carbonic acid 0 (c) Weaker than carbonic acid $+ HCl + HCN \xrightarrow{Anhydrous}$ (d) A neutral compound СНО **103.** Phenol at $25^{\circ}C$ is is known as [MP PET 1997]

	1228 Alcohol, Phe	nol and Ethers			
	(a) Perkin reaction		118.	The final product of the	oxidation of ethyl alcohol
	(b) Gattermann reaction			is	
	(c) Kolbe reaction				[KCET (Med.) 1999]
	(d) Gattermann-Koch rea	action		(a) Ethane	(b) Acetone
112.	Carbylamine test is done	by heating alcoholic <i>KOH</i>		(c) Acetaldehyde	(d) Acetic acid
	with	, ,	119.	with phenol in the	a by heating salicylic acid
	[IIT-JEE 1984	; BIT 1992; CBSE PMT 1992]		oxychloride is	presence of phosphorus
	(a) Chloroform and silve	er powder		0119 011101 1 4 0 10	[KCET (Med.) 1999]
	(b) Trihalogen methane	and primary amine		(a) Salol	(b) Aspirin
	(c) Alkyl halide and prin	nary amine		(c) Oil of wintergreen	(d) o-chlorobenzoyl
	(d) Alkyl cyanide and pr	imary amine		chloride	
113.	Isopropyl alcohol heate	d at 300°C with copper	120.	When phenol is allowed	d to react with Br_2 in (i)
	(a) Acetope	90; MP PMT 1986, 89, 92; JIPA	1ER 20	CS_2 solution and (ii)	in aqueous solution, the
	(a) Acetaldebyde	(d) Ethane		resulting compounds are	2
114.	Dehydrogenation of <i>CH</i> ₂	$-CH - CH_{\circ}$ gives		(a) (i) 2, 4, 6-tribromo	phenol and
	Denyarogenation of ong			(ii) o-and p-bromop	henol
		ОП [MP PMT 2002]		(b) (i) <i>m</i> -bromophenol	and
	(a) Acetone	(b) Acetaldehvde		(ii) 2, 3, 4-tribromo	phenol
	(c) Acetic acid	(d) Acetylene		(c) (i) o-and p-bromoph	ienol and
115.	In the sequence of the fo	llowing reactions		(ii) 2, 4, 6-tribromo	phenol
	$CH_3OH \xrightarrow{HI} CH_3I \xrightarrow{KCN}$			(d) (i) <i>o</i> - and <i>m</i> -bromop	phenol and
	$CH, CN \xrightarrow{\text{reduction}} X \xrightarrow{HNO_3}$	$\rightarrow Y$		(ii) 2, 3, 4-tribromo	phenol
	V_{3} and V_{3} respectively		121.	Which of the followin	g is not true in case of
	(a) CH CH NH and CH			reaction with heated co	pper at 300°C [CPMT 1999]
	(a) $CH_3 CH_2 NH_2$ and CH_3			(a) Phenol \rightarrow Benzyl al	cohol
	(b) $CH_3CH_2NH_2$ and CH_2	₃ COOH		(b) Primary alcohol \rightarrow	Aldehyde
	(c) CH_3CH_2OH and CH_3	СНО		(c) Secondary alcohol –	→ Ketone
	(d) CH_3OCH_3 and CH_3CH_3	НО		(d) Tertiary alcohol \rightarrow	Olefin
116.	Alcohols (i)	$CH_3CH_2CH_2OH$, (ii)	122.	Which of the followi	ng is the most suitable
	$CH_3 - CHOH - CH_3$	and (iii)		ethanol	the traces of water from
	$CH_3 - C(CH_3)(OH) - CH_3$	were treated with Lucas		(a) Heating with Na me	tal
	reagent (Conc. HCl + Zne	Cl_2). What results do you		(b) Passing dry <i>HCl</i> thro	ugh it
	expect at room temperat	ure		(c) Distilling it	Jugii it
	(a) (ii) and (iii) react	immediately and (i) in		(d) Reacting with Mq	
	about 5 minutes		123.	With oxalic acid glycer	ol at 260° C gives [BHII 1006]
	(b) (iii) reacts immediat	tely, (ii) reacts in about 5	50	(a) Allvl alcohol	(b) Glyceryl mono-
	minutes and (1) not a	it all	oxala	ate	
	minutes and (iii) not	at all		(c) Formic acid	(d) Glyceraldehyde
	(d) (i) reacts in about	5 minutes. (ii) reacts in	124.	Absolute alcohol cannot	be prepared by fractional
	about 15 minutes and	l (iii) not at all		distillation of rectified s	spirit since
117.	Ethylene may be obta	ined by dehydration of		(a) It forms azeotropic	mixture
	which of the follow	ving with concentrated		(b) It is used as power a	alcohol
	H_2SO_4 at 160 – 170°C			(c) It is used in wines	
		[DPMT 2000; MP PET 2001]		(d) None of the above	
	(a) C_2H_5OH	(b) <i>CH</i> ₃ <i>OH</i>	125.	The reagent used for	the dehydration of an
	(c) $CH_3CH_2CH_2OH$	(d) $(CH_3)_2 CHCH_2 OH$		alconol 1s	[MD DET/DMT 1000]
					[mr rbi/rmi 1990]

				Alcohol, Phenol a	and Ethers 1229	
	(a) Phosphorus pentach	loride		(d) Lower members l	have pleasant smell and	
	(b) Calcium chloride			burning taste, wh	ile higher members are	
	(c) Aluminium oxide			odourless and taste	less	
	(d) Sodium chloride		134.	At room temperature	the alcohol that do not	
126.	Which one of the folle	owing compounds gives a		reacts with Lucas reage	ent is	
	positive iodoform test	[MP PMT 1997]		(a) Primary alcohol	(b) Secondary alcohol	
	(a) Pentanal	(b) 1-phenyl ethanol		(c) Tertiary alcohol	(d) All these three	
	(c) 2-phenyl ethanol	(d) 3-pentanol	135.	By means of calcium c	hloride which of following	
127.	What amount of bron	nine will be required to		can be dried		
	convert 2 g of phenol in	to 2, 4, 6-tribromophenol[M	P PET/P	Math go granol	(b) Ethanol	
	(a) 4.00	(b) 6.00		(c) Both (a) and (b)	(d) None of these	
_	(c) 10.22	(d) 20.44	136.	Lucas test is used to dis	stinguish between[MP PET 1	
128.	Ethyl alcohol exhibits a	cidic character on reacting		(a) $1^{\circ}, 2^{\circ}$ and 3° alcohomorphic alcohomorphic and 3° alcohomorphic alcohomorphic alcohomorphic and 3° alcohomorphic al	ols (b) 1° , 2° and 3° ami	
	with			(c) Aldehydes and keto	nes (d)Alkenes and alkyn	
	(a) Acotic acid	[MP PM1 1995]	137.	Among the followin	ig, the compound that	
	(a) Acetic aciu			undergoes nitration rea	dily is [NCERT 1984]	
	(b) Souruni metai			(a) Benzoic acid	(b) Toluene	
	(c) Hydrogen Iourde	ahromata		(c) Phenol	(d) Nitrobenzene	
120	(u) Acture potassium un	ul and water connet he	138.	Phenol $\xrightarrow{Z_n} A \xrightarrow{\text{Conc. } H_2S_1}$	$\xrightarrow{O_4} B \xrightarrow{Zn} C$	
129.	separated by distillation	hecause [KCFT 1084]		In the above reaction A	B and C are the following	
	(a) They form a constant	t hoiling mixture		compounds	[MP PMT/PET 1988]	
	(b) Alcohol molecules a	re solvated		(a) $C_6H_6, C_6H_5NO_2$ and	l aniline	
	(c) Their boiling points	are very near		(b) C H dinitrobenze	one and metanitroaniline	
	(d) Alcohol remains dis	solved in water		(c) Taluana matanitral	hongono and mototoluodino	
120	The reaction between a	n alcohol and an acid with		(c) Toluene, metanitrobenzene and metatolued		
130.	the elimination of wate	r molecule is called MH CET	1999]	(u) $C_6 H_6, C_6 H_5 NO_2$ and	i nyurazobenzene	
	(a) Esterification	(b) Saponification	- 139.	$CH_3 - O - C_3H_7$ and C_2H_7	$H_5 - O - C_2 H_5$	
	(c) Etherification	(d) Elimination		exhibit which type of is	omerism	
131.	The compound with the	highest boiling point is		(a) Metamerism	(b) Position	
0	1	[MNR 1985]		(c) Chain	(d) Functional	
	(a) <i>CH</i> ₄	(b) <i>CH</i> ₃ <i>OH</i>	140.	Phenol reacts with CC	l_4 in presence of aqueous	
	(c) $CH_{1}Cl$	(d) CH_{Rr}		alkali and forms a pro	oduct which on hydrolysis	
100	The heiling point of et	hul alashal should be loss		gives	[MP PMT 1990]	
132.	than that of	liyi alconol should be less		(a) Salicylaidenyde	(b) Salicylic acid	
	than that of	[Pb. CET 1985]	1.4.1	(c) Benzaldenyde	(d) Benzoic acid	
	(a) Propane	(b) Formic acid	141.	The fine filter of the felles	indse, alconor and CO_2 are	
	(c) Dimethyl ether	(d) None of these		(a) Chases	(h) Invert sugar	
133.	Which of the followin	g is not characteristic of		(a) Glucose	(d) All of those	
-55*	alcohols	8	140	(c) Fluctose	(u) All of these	
		[AIIMS 1980]	142.	nitrophenol is	Orissa IEE 2003	
	(a) They are lighter tha	n water		(a) $o > m > n$	(b) $p > m > 0$	
	(b) Their boiling points	rise fairly uniformly with		(a) $0 \neq m \neq p$ (c) $m > p > 0$	(d) $p > 0 > m$	
	increasing molecula	r weight	143.	The alcohol which	does not give a stable	
	(c) Lower members ar	e insoluble in water and	-40	compound on dehydrati	ion is [MP PET 1997]	
	organic solvents	but solubility regularly		(a) Ethyl alcohol	(b) Methyl alcohol	
	increases with mole	cular weight		(c) <i>n</i> -propyl alcohol	(d) <i>n</i> -butyl alcohol	
					-	

144. When ethyl alcohol (C_2H_5OH) is mixed with ammonia and passed over heated alumina, the compound formed is

[DPMT 1981; CBSE PMT 1989]

(a) $C_2H_5NH_2$ (b) $C_2 H_4$

(c)
$$C_2H_5OC_2H_5$$
 (d) CH_3OCH_3

- 145. A mixture of methanol vapours and air is passed over heated copper. The products are [KCET 1988]
 - (a) Carbon monoxide and hydrogen
 - (b) Formaldehyde and water vapour
 - (c) Formic acid and water vapour
 - (d) Carbon monoxide and water vapour
- **146.** In the esterification reaction of alcohols[Bihar CEE 1995]
 - (a) OH^- is replaced by CH_3COO group
 - (b) OH^- is replaced by chlorine
 - (c) H^- is replaced by sodium metal
 - (d) OH^- is replaced by C_2H_5OH
- 147. A compound A on oxidation gave acetaldehyde, then again on oxidation gave acid. After first oxidation it was reacted with ammoniacal AgNO₃
 - (a) Primary alcohol (b) Tertiary alcohol
 - (c) Acetaldehyde (d) Acetone
- **148.** Phenol $\xrightarrow{\text{CHCl}_3/\text{NaOH}}$ Salicyldehyde H^+

The above reaction is known as

- (a) Riemer Tiemann reaction
- (b) Bucherer reaction
- (c) Gattermann synthesis
- (d) Perkin reaction
- 149. Alcohol which gives red colour with Victor Meyer test is
 - [RPMT 2003] (a) C_2H_5OH (b) $CH_3 - CH - CH_3$ 0H

(d) None of these (c) $C(CH_3)_3OH$

150. Conc. H_2SO_4 heated with excess of C_2H_5OH at

140 ° C to form[MP PMT 1990; RPMT 2000; AFMC 2002] (a) $CH_3CH_2 - O - CH_3$

- (b) $CH_3CH_2 O CH_2CH_3$
- (c) $CH_3 O CH_2 CH_2 CH_3$
- (d) $CH_2 = CH_2$
- 151. Rate of substitution reaction in phenol is[MP PMT 1989] (a) Slower than the rate of benzene
 - (b) Faster than the rate of benzene
 - (c) Equal to the rate of benzene
 - (d) None of these
- **152.** Phenol reacts with dilute HNO_3 at normal temperature to form [MP PMT 1989]







153. One mole of phenol reacts with bromine to form tribromophenol. How much bromine is used

[MP PMT 1989] (a) 1. 5 mol (b) 3 mol (d) 6 mol (c) 4.5 mol

(b)

154. In presence of *NaOH*, phenol react with $CHCl_3$ to form o-hydroxy benzaldehyde. This reaction is called

> [BIT 1992; MP PMT 1990, 2002; AIIMS 1992; MP PET 1994; JIPMER 1999]

- (a) Riemer-Tiemann's reaction
- (b) Sandmeyer's reaction
- (c) Hoffmann's degradation reaction
- (d) Gattermann's aldehyde synthesis

then silver mirror was produced. A is likely to be[DPMT15996Which of the following vapours passed over heated copper to form acetone [BIT 1992]

(a)
$$H_3C - CH_2 - CH_2OH$$

(b)
$$CH_3 - CH - CH_3$$

[Pb. PMT 2002]

(c)
$$\begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \end{array} C - OH \\ CH_3 \end{array}$$

(d)
$$CH_2 = CH - CH_2OH$$

- 156. 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

157. TNT has the structure









158.	The vapour pressure of methanal is	of a	aqueous	solution	of	
			נט]	PSEAT 200	00]	
	(a) Equal to water	(b)	Equal to :	methanal		
	(c) More than water	(d)	Less than	water		
159.	Glycerol reacts with conc	:. <i>H</i> /	VO_3 and O_3	conc. H_2S	<i>O</i> ₄	
	to form [CPM	T 19	83; MP PN	IT/PET 198	38]	
	(a) Glycerol mononitrate	(b)	Glycerol	dinitrate		169.]
	(c) Glycerol trinitrate	(d)	Acrolein]
160.	Glycerol heated with oxal	lic a	cid at 110	^{o}C to for	m	
	[CPMT 198	6, 90	o, 91, 97; J	IPMER 19	97]	
	(a) Formic acid	(b)	Oxalic ac	id		
	(c) Allyl alcohol	(d)	Glycerol	trioxalate		170.
161.	Dimethyl ether and ethyl	alco	ohol are			
	[CPM]	T 198	36; Manip	al MEE 199	95]	
	(a) Branched isomer	(b)	Position i	somer		
_	(c) Functional isomer	(d)	Tautome			171
162.	The process of manufac	ture	e of abso	lute alco	hol	1/1.
	from rectified spirit is[CF	РМТ	1986, 87;	Kurukshet	ra CEE	2002]
	(a) Fractional distillation	1	(d)Vacuu	n distillati	lon	
160	When other alcohol road	II ctc t	with acou	in uistilla	bo	152
103.	products formed are		with acei	IC delu, i		1/2.
	(a) Sodium ethovide \pm hy	dro	σen		59]	
	(h) Ethyl acetate + water	, ui 0,	gen			
	(c) Ethyl acetate $+$ soan					
	(d) Ethyl alcohol $+$ water					
_	(u) Ethyl alcohol + water					173.
164.	Picric acid is (at $25^{\circ}C$)					-/3
	(a) A white solid	(b)	A colourl	ess liquid		
	(c) A gas	(d)	A bright	yellow sol	ıd	
165.	Phenol on distillation wit		nc dust gi			
	[MP PET 1991; CPM1	199	7; MP PM	1 1999, 20 h DMT 200	01; 00]	
	(a) $C_{\cdot}H_{\cdot}$	(h)	C.H.	0. FWII 200	101	184
			C ₆ 11 ₁₂			1/4.
	(c) $C_6 H_5 O C_6 H_5$	(d)	$C_6H_5 - C_6$	${}_{6}H_{5}$		1
166.	Methanol and ethanol are	e mi	scible in v	water due	to	
	[MP PET/PMT 1988; C	РМТ	1989; CB	SE PMT 19	91]	
	(a) Covalent character					175.
	(b) Hydrogen bonding ch	arac	ter			1
	(c) Oxygen bonding chara	acte	r			
_	(d) None of these					
167.	By distilling glycol with	n fu	ming sul	phuric ac	id,	176.
	which of following is obta	aine	d			
	(a) Glycerol	(b)	Pinacol			
	(c) Dioxan	(d)	Ethylene	oxide		177.
168.	The compound which carbonium ion on dehydr	give atio	es the 1 n is	most stal [DCE 200	ble Do]	,,
	(a) $CH_3 - CH - CH_2OH$					
	CH_{2}					178.
	- 3					-

(b)	$CH_3 - C - OH$			
	CH ₃			
(c)	$CH_3 - CH_2 - CH_2 - CH_2$	$-CH_2OH$		
	CH ₃			
(d)	$CH_3 - CH - CH_2 -$	CH ₃		
In	CH_3CH_2OH	which	bond	dissociates
hete	erolytically			
		[IIT-	-JEE 1988	; CPMT 1996]
(a)	C - C	(b) (C – O	
(c)	С – Н	(d) (0 – H	

 CH_3

- Which compound is soluble in water
 - [IIT-JEE 1980; CPMT 1993; RPET 1999]

- (a) CS_2 (b) C_2H_5OH
- (c) CCl_4 (d) $CHCl_3$
- Which of the following is most soluble in water [MP PMT 1995]
 - (a) Normal butyl alcohol (b) Isobutyl alcohol
 - (c) Tertiary butyl alcohol (d)Secondary butyl alcohol
- Which of the following gives negative iodoform test

(a)
$$CH_3CH_2OH$$
 (b) $CH_3CH_2CH_2OH$
(c) $C_6H_5-CH-CH_3$ (d) $CH_3-CH-CH_3$
 OH

If ethanol dissolves in water, then which of the following would be done [MP PET 1989]

- (a) Absorption of heat and contraction in volume
- (b) Emission of heat and contraction in volume
- (c) Absorption of heat and increase in volume
- (d) Emission of heat and increase in volume
- A migration of hydrogen with a pair of electrons is called
 - (a) Alkyl shift (b) Hydride shift
 - (c) Hydrogen ion formation (d) Dehydrogenation
- When rectified spirit and benzene are distilled together, the first fraction obtained is
 - (a) A ternary azeotrope (b) Absolute alcohol
 - (c) A binary azeotrope (d) Denatured spirit
- Alcohols react with Grignard reagent to form[DPMT 1986]
 - (a) Alkanes (b) Alkenes
 - (c) Alkynes (d) All of these
- Action of diazomethane on phenol liberates
 - (a) *O*₂ (b) *H*₂ (c) N_2 (d) CO_{2}

 - The ring deuteration of phenol
 - (a) Lowers the acidity
 - (b) Increases the acidity
 - (c) Imparts no effect

	(d) Causes amphoteric n	nature		(a) Ethane	(b) Ethylene
179.	In esterification of an ac	cid, the other reagent is		(c) Butane	(d) Propane
		[CPMT 1988]	191.	Diethyl ether absorbs or	xygen to form [DPMT 1984]
	(a) Aldehyde	(b) Alcohol		(a) Red coloured sweet	smelling compound
	(c) Amine	(d) Water		(b) Acetic acid	
180.	Maximum solubility of a	lcohol in water is due to		(c) Ether suboxide	
	[MP PM	IT/ PET 1988; MP PMT 1989]		(d) Ether peroxide	
	(a) Covalent bond	(b) Ionic bond	192.	Diethyl ether can be deo	composed by heating with
	(c) <i>H</i> -bond with H_2O	(d) None of the above			[CPMT 1980, 81, 89]
181.	Alcohols can be distingu	ished from alkenes by		(a) HI	(D) NaOH
	(a) Dissolving in cold co	oncentrated H_2SO_4		(c) water	(u) $KMnO_4$
	(b) Decolourizing with t	promine in CCl_{A}	193.	On boiling with concer	ntrated hydrobromic acid,
	(c) Oxidizing with neutr	ral permanganate solution		pnenyl etnyl etner will	yield [AIIMS 1992]
	(d) None of the above	ai permanganate solution		(a) Phenol and ethyl bro	omide
400	(u) None of the above $A = 25^{\circ}C$. Etherland above	·		(b) Prienoi and ethane	othanal
182.	At 25 C Ethylehe grycol	(b) Liquid		(d) Bromobenzene and	ethano
	(a) Sond compound	(d) Drown colid	104	Ether is formed when e	thyl alcohol is heated with
100	(C) Gas	(d) Brown sond	194.	conc. H_2SO_4 . The condi	itions are [KCET 1984]
183.	produces	s oxidised with chiorine, it		(a) Frances (11.60	
	produces	[AFMC 1000]		(a) Excess of $H_2 SO_4$ and	la 1/0°C
	(a) HCHO	(b) <i>CH</i> ₂ <i>CHO</i>		(b) Excess of C_2H_5OH a	and 140 ° C
	(c) CCl_3CHO	(d) C_3H_7CHO		(c) Excess of C_2H_5OH a	and 180 ° C
184	Alcohols combine with	acetylene in the presence		(d) Excess of conc. H_2S	O_{4} and $100^{o}C$
104.	of mercury compounds a	as catalyst to form	105.	The ether	
	(a) Acetals	(b) Xanthates	-99		
	(c) Vinyl ethers	(d) None of the above		when treated with HI n	roduces
185.	The compound which w	ill give negative iodoform		when treated with m p	iouuces
•	test is	5 5		(a) $(-CH_{a})$	(b) (H,OH)
		[CPMT 1993, 99]			
	(a) CH_3CHO	(b) CH_3CH_2OH			
	(c) Isopropyl alcohol	(d) Benzyl alcohol		(c) <u> </u>	(d)
186.	Which of the following i	s most acidic [CPMT 1999]	196.	Addition of alcohols to	aldehydes in presence of
	(a) Phenol	(b) Benzyl alcohol	-	anhydrous acids yield	[CET Pune 1998]
	(c) <i>m</i> -chlorophenol	(d) Cyclohexanol		(a) Carboxylic acids	(b) Ethers
187.	Number of metamers	represented by molecular		(c) Cyclic ethers	(d) Acetals
	formula $C_4 H_{10} O$ is	[Tamil Nadu CET 2001]	197.	In which of the follo	wing reaction, phenol or
	(a) 4	(b) 3		sodium phenoxide is no	t formed [CPMT 1996]
	(c) 2	(d) 1		(a) $C_6H_5N_2Cl + alco.KOH$	$H \rightarrow$
188.	When ether is exposed	l in air for sometime an		(b) $C_6H_5OCl + NaOH \rightarrow$	
	explosive substance pro	duced is [RPMT 2002]		(c) $C_6H_5N_2Cl + aq. NaOH$	$l \rightarrow$
	(a) Peroxide	(b) TNT		(d) $C H NNC H_2^0$	
	(c) Oxide	(d) Superoxide		(u) $C_6 H_5 NNCl \xrightarrow{\Delta}$	
189.	Ether which is liquid at	room temperature is[BVP 200	² 198.	Dimethyl ether when he	eated with excess <i>HI</i> gives
	(a) $C_2H_5OCH_3$	(b) CH_3OCH_3			[CPMT 1996]
	(c) $C_2H_5OC_2H_5$	(d) None of these		(a) CH_3I and CH_3OH	
190.	In the following reaction	1		(b) CH_3I and H_2O	
	$C_2H_5OC_2H_5 + 4[H] - \frac{\text{Red P}}{1}$	$\xrightarrow{\text{HI}} 2X + H_2O, X \text{ is}$		(c) $C_2H_6 + CH_3I$ and CH_6	H ₃ OH
	2 J 2 J E I	[MP PMT 2002]		(d) CH_3I and $HCHO$	
		[

c)	Water (d)	K	MnO_4		
)n bhe	boiling with concentrate enyl ethyl ether will yield	ed	hydro	bromic [AIIMS 1	acid, 1 992]
a)	Phenol and ethyl bromide	9			
b)	Phenol and ethane				
c)	Bromobenzene and ethan	ol			
d)	Bromobenzene and ethan	e			
Eth	er is formed when ethyl a	alc	ohol is	heated	with
on	ic. H_2SO_4 . The conditions	a	re	[KCET 1	984]
a)	Excess of H_2SO_4 and 170) ^o (C		
b)	Excess of C_2H_5OH and 1	40	°C		
c)	Excess of C_2H_5OH and 1	80	°C		
d)	Excess of conc. H_2SO_4 as	nd	$100 \circ C$		
-1					

5. The ether
$$0 - CH_2$$

(a)
$$\swarrow$$
 $-CH_2I$ (b) \checkmark $-CH_2OH$
(c) \checkmark $-I$ (d) \checkmark $-OH$

- of alcohols to aldehydes in presence of us acids yield [CET Pune 1998]
 - oxylic acids (b) Ethers
 - ic ethers (d) Acetals
- h of the following reaction, phenol or phenoxide is not formed [CPMT 1996] $_{5}N_{2}Cl + alco. KOH \rightarrow$
 - $_{5}OCl + NaOH \rightarrow$
 - $_{5}N_{2}Cl + aq. NaOH \rightarrow$

(d)
$$C_6H_5NNCl \xrightarrow{H_2O}_{\Delta}$$

- I and H_2O
- $_{6} + CH_{3}I$ and $CH_{3}OH$
- I and HCHO

199. The ether that undergoes electrophilic substitution reactions is [JIPMER 2001] (a) $CH_3OC_2H_5$ (b) $C_6H_5OCH_3$

(c)
$$CH_3OCH_3$$
 (d) $C_2H_5OC_2H_5$

- **200.** Acetyl chloride does not react with [MNR 1995] (a) Diethyl ether (b) Aniline
 - (c) Phenol (d) Ethanol
- **201.** The products formed in the following reaction $C_6H_5 - O - CH_3 + HI \xrightarrow{\text{heat}} \text{are}$ [IIT 1995]
 - (a) $C_6H_5 I$ and $CH_3 OH$
 - (b) $C_6H_5 OH$ and $CH_3 I$
 - (c) $C_6H_5 CH_3$ and HOI
 - (d) $C_6 H_6$ and $CH_3 OI$
- **202.** Etherates are
 - (a) Ethers
 - (b) Solution in ether
 - (c) Complexes of ethers with Lewis acid
 - (d) Complexes of ethers with Lewis base
- 203. An ether is more volatile than an alcohol having the same molecular formula. This is due to[AIEEE 2003]
 - (a) Dipolar character of ethers
 - (b) Alcohols having resonance structures
 - (c) Inter-molecular hydrogen bonding in ethers
 - (d) Inter-molecular hydrogen bonding in alcohols
- **204.** When ether is reacted with O_2 , it undergoes explosion due to [CPMT 1996] (a) Peroxide (b) Acid

(d) TNT (c) Ketone

205. The compound which does not react with sodium is

	[CBSE PMT 1994]
(a) $C_2 H_5 OH$	(b) $CH_3 - O - CH_3$
(c) CH_3COOH	(d) $CH_3 - CHOH - CH_3$

- 206. Methyl-terbutyl ether on heating with HI of one molar concentration gives [MP PET 1997]
 - (b) $CH_3OH + (CH_3)_3Cl$ (a) $CH_3I + (CH_3)_3COH$
 - (c) $CH_{3}I + (CH_{3})_{3}Cl$ (d) None of the above
- **207.** A substance $C_4 H_{10}O$ yields on oxidation a compound $C_4 H_8 O$ which gives an oxime and a positive iodoform test. The original substance on treatment with conc. H_2SO_4 gives C_4H_8 . The structure of the compound is [SCRA 2000] (a) $CH_3CH_2CH_2CH_2OH$
 - (b) $CH_3CH(OH)CH_2CH_3$
 - (c) $(CH_3)_3 COH$
 - (d) $CH_3CH_2 O CH_2CH_3$
- **208.** Ethylene glycol reacts with excess of *PCl*₅ to give

[Kerala PMT 2004]

[CPMT 2004]

- (a) 1, 1-dichloroethane
- (b) 1, 2-dicholoroethane
- (c) 1, 1, 1-trichloroethane
- (d) 1, 1, 2, 2-tetrachloroethane
- (e) 2, 2-dichloroethane

(

a)
$$O_2N \xrightarrow{OH} NO_2$$

NO₂ (b) C_2H_5OH

(c)
$$CH_3CONH_2$$
 (d) $CH(CN)$

- **210.** The boiling point of methanol is greater than that of methyl thiol because [Kerala PMT 2004]
 - (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
 - (e) There is no hydrogen bonding in methanol and intramolecular hydrogen bonding in methyl thiol

$$CH_2OH$$

- $\begin{array}{c} & COOH \\ CHOH + & \\ CHOH + & \\ COOH \end{array} \xrightarrow{110^{\circ}C} (A) \text{ product} \\ CH_2OH \end{array}$ **211.** In the reaction *CHOH* +
 - (A) will be
 - (a) Glycerol monoformate
 - (b) Allyl alcohol
 - (c) Formaldehyde
 - (d) Acetic acid
- 212. Which of the following will not form a yellow precipitate on heating with an alkaline solution of iodine

[CBSE PMT 2004]

[Pb.CET 2001]

- (a) CH_3OH
- (b) CH_3CH_2OH
- (c) $CH_3CH(OH)CH_3$
- (d) $CH_3CH_2CH(OH)CH_3$
- 213. In Friedal-Crafts acylation, besides AlCl₃, the other reactants are [DPMT 2004]





	1234 Alcohol, Phe	enol and Eth	iers			
(a	$+CH_3Cl$	(b)	+CH ₃ COCl	224.	Fats, on alkaline hydroly	ysis, gives [MH CET 2003]
					(a) Oils	(b) Soaps
		<u>^</u>			(c) Detergents	(d) Glycol + acid
(6)				225.	When vapours of an al	cohol are passed over hot
	$+HN_3$		$+CH_3Cl$		reduced copper, alcoho	l is converted into alkene
4. W	hich of the followin	ng reagents	will produce		quickly, the alcohol is	[CPMT 1985]
sa	licyldehyde on reaction	on with phen	ol[DPMT 2004]		(a) Primary	(b) Secondary
(a) $CHCl_3 / NaOH$	(b) CCl_4 / N	laOH		(c) Tertiary	(d) None of these
(c) $CH_2Cl_2 / NaOH$	(d) <i>CH</i> ₃ <i>Cl</i> /	NaOH	226.	The adduct of the compreaction with excess	pound 'A' obtained by the of isopropyl magnesium
5. At pr	530 <i>K</i> , glycerol re roduce	eacts with o	oxalic acid to		iodide, upon hydrolysis The compound ' A ' is	gives a tertiary alcohol.
•			[Pb. CET 2002]		The compound if is	[MP PET 1085]
(a) Allyl alcohol	(b) Formic	acid		(a) An ester	(b) A secondary alcohol
(c) Glyceraldehyde	(d) Glycero	01		(c) A primary alcohol	(d) An aldehyde
noox	kalate			227	If there be a compound	of the formula $CH C(OH)$
5. W	ith anhydrous zinc	chloride, et	hylene glycol	22/.	which one of the follow	wing compounds would be
gi	ves				obtained from it wit	hout reaction with any
		I	[MP PMT 2004]		reagent	[CPMT 1983]
(a) Formaldehyde	(b) Acetyle	ne		(a) <i>CH_OH</i>	(b) <i>C₂H₂OH</i>
(c) Acetaldehyde	(d) Acetone	2			(d) UCUO
•. W	hich of the following	ig compound	l give yellow		(c) CH_3COOH	(u) <i>HCHO</i>
pr	recipitate with I_2 and	NaOH	[Pb. CET 2003]	228.	Which of the following	can work as a dehydrating
(a) <i>СН</i> ₃ <i>ОН</i>	(b) <i>CH</i> ₃ <i>CH</i>	$_2CH_2OH$		agent for alcohols	[BHU 1980]
(c) $C_2H_5OC_2H_5$	(d) CH_3CH_3	$_2OH$		(a) $H_2 SO_4$	(b) Al_2O_3
3. Ar	nongst the following,	HBr reacts fa	astest with		(c) $H_3 PO_4$	(d) All of these
	[IIT-JEE 19	86; JIPMER 20	000; DCE 2003]	229.	What is formed when gl	ycerol reacts with <i>HI</i> [DCE 2
(a) Propane-1-ol	(b) Propan	e-2-ol		CH_2OH	CH_2
(c) 2-methyl propane-1-	-ol (d)2-m	ethyl propane-2-	ol	(a) CHI	(b) <i>CH</i>
). W	hich of the following	react with b	enzoic acid to			
fo	rm ethyl benzoate		[Pb. CET 2001]		СН	сн он
(a) Ethyl alcohol	(b) Cinnam	ic acid		CH_3	(1)
(c) Sodium ethoxide	(d) Ethyl c	hloride		(c) CH_2	(d) $C = O$
). W	hen phenyl magnesiu	ım bromide	reacts with <i>t</i> -		CH_3	CH ₃
bu	itanol, the product wo	ould be		230.	The dehydration of 2-n	nethyl butanol with conc.
(a) Benzene	(b) Phenol	_		H_2SO_4 gives	[UPSEAT 2004]
(c) <i>t</i> -butyl benzene	(d) <i>t</i> -butyl	ether		(a) 2-methyl butene as i	najor product
. W	hich of the followin	g is used a	s catalyst for		(b) Pentene	
pr	eparing Grignard reag	gent	[Pb. CET 2002]		(c) 2-methyl but-2-ene a	as major product
(a) fron powder	(b) Dry eth	er		(d) 2-methyl pent-2-ene	
(C) Activated charcoal	(d) MnO_2		231.	Which alcohol reacts wi	th fatty acids to form fats
2. Et	hyl alcohol is heate	d with conc	H_2SO_4 . The		[MP P	MT/PET 1988; MP PET 1991]
pr	oduct formed is		[DCE 2004]		(a) Ethanol	(b) Glycerol
	<i>O</i>				(c) Methanol	(d) Isopropanol
(a	$CH_3 - C - OC_2H_5$	(b) $C_2 H_6$		232.	Which will dehydrate ea	Isily [Roorkee 1995]
(c	C_2H_4	(d) $C_2 H_2$			(a) 3-methyl-2-butanol	(b) Ethyl alcohol
3. De	ehvdration of 2-butan	ol vield	[Ph. CET 2004]		(c) 2-methyl propane-2-	ol (d)2-methyl butanol-2
ى ر د)) 1-butene	(h) 2-hitter	L 0, CEI 2004]		*	-
(a) 2-but we a	(d) Poth (a) and (b)			
	j ⊿-butylle	(u) DULII (a) allu (D)			

Alcohol,	Phenol	and	Ethers	1235
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+HBr —

(d)

- Al_2O_3 Си $-CH_3CH_2OH$ $\rightarrow B.$ Α and R **233.** *A*← respectively are [RPMT/PET 2000] (b) Alkyne, alkanal (a) Alkene, alkanal
 - (c) Alkanal, alkene (d) Alkene, alkyne
- 234. Which one of the following reactions would produce secondary alcohol [MP PET 1994] 0

(a)
$$C_6H_5CCH_3 \xrightarrow{1.CH_3MgBr}_{2.H^+}$$

 O
(b) $C_6H_5CCH_3 \xrightarrow{1.LiAlH_4}_{2.H^+}$
(c) $CH_3CHO \xrightarrow{1.LiAlH_4}_{2.H^+}$
(d) $CH_3CCH_3 \xrightarrow{1.OH^-}_{2.Br}$

235. On reaction with hot conc. H_2SO_4 , which one of the following compounds loses a molecule of water

[CPMT 1989]

- (a) CH_3COCH_3 (b) CH₃COOH
- (c) CH_3OCH_3 (d) CH_3CH_2OH
- 236. The best method to prepare cyclohexene from cyclohexanol is by using [IIT 2005] (a) Conc. $HCl + ZnCl_2$ (b) Conc. H_3PO_4 (c) HBr (d) Conc. HCl
- 237. Which of the following compound is most acidic [BCECE 2005]
 - (a) CH_4 (b) $C_2 H_6$

(c)
$$CH \equiv CH$$
 (d) C_2H_5OH

- **238.** C_2H_5OH can be differentiated from CH_3OH by
 - [MP PMT 1994] (a) Reaction with HCl (b) Reaction with NH_3
 - (c) By iodoform test (d) By solubility in water
- 239. A compound does not react with 2.4 dinitrophenyl hydrazine and Na , compound is[UPSEAT 2003] (a) Acetone (b) Acetaldehyde
 - (c) CH_3OH (d) $CH_2 = CHOCH_3$
- 240. Which of the following reaction is correctly represented





- 243. In which of the following reactions carbon carbon bond formation takes place [DPMT 2005] (a) Cannizzaro (b) Reimer-Tiemann
 - (c) HVZ reaction (d) Schmidt reaction
- **244.** Reaction of phenol with chloroform/sodium give hydroxide to o-hydroxy benzaldehyde involves the formation of

[] & K 2005]

 $+CH_3Br$

- (a) Dichloro carbene (b) Trichloro carbene
- (c) Chlorine atoms (d) Chlorine molecules
- **245.** Which is not correct [J & K 2005]
 - (a) Phenol is more acidic than acetic acid
 - (b) Ethanol is less acidic than phenol
 - (c) Ethanol has lower boiling point than ethane
 - (d) Ethyne is a non-linear molecule

Uses of alcohol, Phenol and Ethers

- Glycerol is used in the manufacture of [SCRA 1991] 1. (a) Dynamite (b) Varnish
 - (c) Paints (d) Soft drinks
- Glycerol as a triester present in 2. [MP PMT 1990] (a) Petroleum (b) Kerosene
 - (c) Vegetable oil and fat (d) Naphtha
- In presence of air, fermentation of ethyl alcohol 3. by azotobactor bacteria forms [MP PMT 1989]
 - (a) $CH_2 = CH_2$
 - (c) CH_3CHO (d) CH_3COOH
- Aspirin is also known as[CPMT 1989, 94; MP PET 1995] 4. (a) Methyl salicylic acid (b) Acetyl salicylic acid (c) Acetyl salicylate (d) Methyl salicylate
- (b) $C_2 H_6$

	1236 Alcohol, Ph	enol and Ethers				
5.	Substances used i	n bringing down the		(c) As an antifreeze fo	r water	(d)
	temperature in high fe	vers are called [DPMT 1983]	17.	Liquor poisoning is du	e to	[CPMT 1971]
	(a) Pyretics	(b) Antipyretics		(a) Presence of bad co	mpound in liqu	ior
	(c) Antibiotics	(d) Antiseptics		(b) Presence of methyl	alcohol	
6.	When glycol is heated	with dicarboxylic acid, the		(c) Presence of ethyl a	lcohol	
	products are			(d) Presence of carbon	ic acid	
	(a) Polyesters	(b) Polyethers	10	In order to make alcoh	le aciu	nuriding and
	(c) Polyethylene	(d) No reaction at all	10.	methanol are added to	of unul mkable	ing alcohol is
7.	Cresol is	[BHU 1996]		called	it. The result	ing alcohol 15
	(a) A mixture of three	cresols with little phenol		(a) Power alcohol	(b) Proof sr	virit
	(b) Used as dye for wo	od		(a) Denatured spirit	(d) Poison :	lcohol
	(c) A soapy solution of	cresols	10	(c) Denatured spirit	inly used as a	
	(d) Having an aldehyd	e group	19.	Denatured spirit is ma	inty used as a	
8.	Phenol is used in the m	nanufacture of [AIIMS 1996]		(a) Candfuel	[MNR 1995;	MP PET 2002]
	(a) Bakelite	(b) Polystyrene		(a) Good fuel		
	(c) Nylon	(d) PVC		(b) Drug		
9.	In cold countries ethyl	ene glycol is added to water		(c) Solvent in preparir	ıg varnishes	
	in the radiators to[CPM	IT 1971; NCERT 1971; MP PMT 19	93]	(d) Material in the pre	paration of oil	
	(a) Bring down the spe	ecific heat of water	20.	Main constituent of dy	namite is [MP	PET 1992; BHU 197
	(b) Lower the viscosity	Į		(a) Nitrobenzene	(b) Nitrogly	cerine
	(c) Reduce the viscosit	У		(c) Picric acid	(d) TNT	
	(d) Make water a bette	er lubricant	21.	Wine (alcoholic bevera	ıges) contains	
10.	Power alcohol is	[KCET 1990]		[CPMT 19	72, 77; BHU 199	6; AFMC 2001]
	(a) An alcohol of 95%	purity		(a) CH_3OH	(b) Glycerol	L
	(b) A mixture of petrol	hydrocarbons and ethanol		(c) C_2H_5OH	(d) 2-propa	nol
	(c) Rectified spirit		22.	Tonics in general conta	ain	[MNR 1995]
	(d) A mixture of metha	anol and ethanol		(a) Ether	(b) Methan	ol
11.	4-chloro-3, 5-dimethyl	phenol is called[KCET 2003]		(c) Ethanol	(d) Rectifie	d spirit
	(a) Chloramphenicol	(b) Paracetamol	23.	Widespread deaths du	e to liquor poi	soning occurs
	(c) Barbital	(d) Dettol		due to		
12.	Alcoholic fermentation	n is brought about by the				[DPMT 2001]
	action of			(a) Presence of carbon	ic acid in lique	r
	(a) (0)	(h) ()		(b) Presence of ethyl a	Iconol in liquo	r
	(a) CO_2	$(0) O_2$		(c) Presence of methyl	alcohol in liqu	lor
	(c) Invertase	(d) Yeast	~ ^	(d) Presence of lead co	mpounds in 110	luor
13.	Rectified spirit is a min	xture of	24.	Dietnyl etner finds use	(h) A huma	5 [KCET 1989]
	LDPM	IT 1982; MP PMT 1976, 77, 96;		(a) A pain kiner	(d) A hypho	the
	(a) 05% ethyl alcohol	- 50% water	25	Washing soan can be	(u) All allae	silletic
	(a) 95% ethyl alcohol	+ 570 water	23.	with alkali of the oil	prepared by s	[CPMT 1086]
	(c) 04.4% ethyl alcoho	+ 4.5370 water		(a) Rose oil	(b) Paraffin	oil
	(d) $0 = 57\%$ ethyl alcoh	n + 5.45% water		(c) Groundnut oil	(d) Kerosen	e
14	Methyl alcohol is toxic	The reason assigned is $\mathbf{P}\mathbf{P}\mathbf{T}$	a 26 .1	Ether can be used	(u) neroben	CPMT 1982]
14.	(a) It stops respirators	v track	2000]	(a) As a general anaes	thetic (b) As	a refrigerant
	(a) It stops respiratory	f that f_{i} and f_{i} and f_{i} and f_{i} and f_{i}		(c) In perfumery	(d) All of th	ese
	(b) It reacts with niti	rogen and forms CN in the	27.	The Bouveault-Blanc re	eduction involv	ves[MP PET 1991]
	(a) It increases (C)	optopt in the blood		(a) $C_2 H_5 OH / Na$	(b) LiAlH	
	(c) it increases CO_2 C			(c) $C H M \sim V^{-}$	$(d) \overline{\mathcal{I}}_{\alpha} / \overline{\mathcal{I}}_{\alpha} / \overline{\mathcal{I}}_{\alpha}$	
	(d) It is a reduction pr	oduct of formaldehyde		$C_2 \Pi_5 MgX$	(u) Zn/HCl	
15.	Glycerol is used	[Kurukshetra CET 2002]	28.	Which is used as an an	tifreeze	[AFMC 1992]
	(a) As a sweetening ag	ent		(a) Glycol	(b) Ethyl al	cohol
	(b) In the manufacture	ot good quality soap		(c) Water	(d) Methano)]
	(c) In the manufacture	of nitro glycerine				
	(d) In all of these			C Critica	al Thinl	ling
16.	Glycerol is not used in	which of following cases			ai i i i i i i i i i i i i i i i i i i	NHY
	(a) Evalocivo malving	(b) Shawing coan making				

16. Glycerol is not used in which of following cases (a) Explosive making (b) Shaving soap making

Objective Questions

1. Which will undergo a Friedel-Craft's alkylation reaction



10. Propan-1-ol can be prepared from propene by alcohol

[AIIMS 2003]

- (b) $Hg(OAc)_2 / H_2O$ followed by $NaBH_4$
- (c) B_2H_6 followed by H_2O_2
- (d) CH_3CO_2H/H_2SO_4

(a) H_2O/H_2SO_4

- 11. Distinction between primary, secondary and tertiary alcohol is done by[MP PMT/PET 1988; RPMT 2000] (a) Oxidation method
 - (b) Lucas test
 - (c) Victor Meyer method
 - (d) All of these
- 12. Oxidation of which of the following by air in presence of vanadium pentoxide gives phenol (a) Toluene (b) Benzene
 - (c) Benzaldehyde (d) Phenyl acetic acid
- **13.** The most suitable method of the separation of a 1 : 1 mixture of *ortho* and *para* nitrophenols is
 - [CBSE PMT 1994, 99; CPMT 1997]
 - (a) Distillation (b) Sublimation
 - (c) Crystallization (d) Chromatography
- **14.** Which of the following does not form phenol or phenoxide

[AFMC 2000]

- (a) C_6H_5Cl (b) C_6H_5COOH (c) $C_6H_5N_2Cl$ (d) $C_6H_5SO_3Na$
- 15. Which of the following will be obtained by keeping ether in contact with air for a long time[RPMT 20 (a) C₂H₅ O CH (CH₃) O OH
 - (b) $C_2H_5 OCH_2 OH$
 - (c) $C_2H_5 O C_2H_5OH$
 - (d) $CH_3 O CH (CH_3) O OH$
- 16. When a mixture of ethanol and methanol is heated in the presence of concentrated H₂SO₄ the resulting organic product or products is/are[Manipal MEE (a) CH₃OC₂H₅
 - (b) CH_3OCH_3 and $C_2H_5OC_2H_5$
 - (c) $CH_3OC_2H_5$ and CH_3OCH_3
 - (d) $CH_3OC_2H_5$, CH_3OCH_3 and $C_2H_5OC_2H_5$
- **17.** In the following groups

-OAc	-OMe	$-OSO_2Me$	$-OSO_2CF_3$
Ι	II	III	IV
The order	of leaving gro	oup ability is	[IIT 1997]
(a) I > II :	> III > IV		

- (b) IV > III > I > II
- (c) III > II > I > IV
- (d) II > III > IV > I

18. Epoxides are

- (a) Cyclic ethers
- (b) Not ethers
- (c) Aryl-alkyl ethers
- (d) Ethers with another functional group

19.	The reaction of $CH_3CH = CH$	ОН
	with <i>HBr</i> gives	[IIT-JEE 1998]
	(a) $CH_{2}CHBrCH_{2} \longrightarrow OH$	

(b)
$$CH_3CH_2CHBr$$
 OH

- (c) $CH_3CHBrCH_2 \longrightarrow Br$ (d) $CH_3CH_2CHBr \longrightarrow Br$
- **20.** Which of the following compounds on boiling with $KMnO_4$ (alk.) and subsequent acidification will not give benzoic acid [KCET 2001] (a) Benzyl alcohol (b) Acetophenone (c) Anisole (d) Toluene
- 21. The best reagent to convert pent-3-en-2-ol into
pent-3-in-2-one is[AIEEE 2005](a) Acidic permanganate
 - (b) Acidic dichromate
 - (c) Chromic anhydride in glacial acetic acid
 - (d) Pyridinium chloro-chromate
- **22.** When alcohol reacts with concentrated H_2SO_4 intermediate compound formed is [AFMC 2005] 1
 - (a) Carbonium ion (b) Alkoxy ion
 - (c) Alkyl hydrogen sulphate (d) None of these

Assertion & Reason For ANMS Aspirants

Read the assertion and reason carefully to mark the correct option out of the options given below:

- (a) If both assertion and reason are true and the reason is the correct explanation of the assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of the assertion.
- (c) If assertion is true but reason is false.
- (d) If the assertion and reason both are false.
- (e) If assertion is false but reason is true.

1.	Assertion	A triester of glycerol and palmitic acid on boiling with aqueous <i>NaOH</i>							
		gives a solid cake llav	ing soapy touch						
	Reason :	Free glycerol is liber	ated which is a						
		greasy solid [AIIMS 1996							
2.	Assertion	: Phenol is a weak act	d than etnanol						
	Reason :	Groups with + M effe	ct and – I effect						
		decrease acidity at <i>p</i> -p	osition[AIIMS 2002]						
3.	Assertion	: Phenol is more	reactive than						
		benzene towards	electrophilic						
		substitution reaction							

	Reason :	In the case of phenol, the intermediate carbocation is more resonance stabilized
4.	Assertion	[IIT-JEE (Screening) 2000] : Phenol undergo Kolbe reaction, ethanol does not.
	Reason :	Phenoxide ion is more basic than ethoxide ion. [AIIMS 1994]
5.	Assertion	: Lucas reagent is a mixture of anhydrous <i>ZnCl</i> ₂ and concentrate <i>HCl</i>
	Reason :	Primary alcohol produce ppt. with Lucas reagents. [AIIMS 1995]
6.	Assertion	: Resorcinol turns $FeCl_2$ solution
	Deces	Personal have abarable mount fattage and a
7.	Assertion :	: Glycerol is purified by distillation
	Deces	Character reduced pressure.
0	Accortion	Alcohol and phonol con ho
0.	Rongon i	distinguished by sodium hydroxide.
noutr	Reason :	Phenol is acture while alcohol is
	di.	· Alcohola are debudrated to
9.	ASSELLIOII	hydrocarbons in the presence of acidic zeolites.
	Reason :	Zeolites are porous catalysts.
10.	Assertion	: The major products formed by heating $C_6H_5CH_2OCH_3$ with <i>HI</i> are
		C_6H_5CH, I and CH_3OH .
	Reason :	Benzyl cation is more stable than methyl cation. [AIIMS 2004]
11.	Assertion	: The <i>pka</i> of acetic acid is lower than that of phenol.
- 4 - 1. * 1	Reason :	Phenoxide ion is more resonance
stabil	lized.	[AIIMS 2004]
12.	Assertion	: Alcoholic fermentation involves conversion of sugar into ethyl alcohol by yeast.
	Reason :	Fermentation involves the slow decomposition of complex organic
13.	Assertion	: The water solubility of the alcohols follow the order <i>t</i> -butyl > <i>s</i> -butyl alcohol > <i>n</i> -butyl alcohol.
	Reason :	Alcohols form <i>H</i> -bonding with water to show soluble nature.
14.	Assertion	: Absolute ethanol can be obtained by simple fractional distillation of a mixture of alcohol and water.
	Reason :	The absolute alcohol boils at 78.3°C.
15.	Assertion	: Acid catalysed dehvdration of <i>t</i> -
		butanol is slower than <i>n</i> -butanol.
	Reason :	Dehydration involves formation of the protonated alcohol, ROH_2^+ .
16.	Assertion	: Tertiary alcohols give turbidity
	Reason :	A mixture of conc. <i>HI</i> + anhydrous
		$ZnCl_{2}$ is called Lucas reagent.

17.	Assertion	: 4-nitrophenol is more acidic than 2,
	Reason :	Phenol is a weaker acid than carbonic
acid.		
18.	Assertion	: Phenols cannot be converted into
		esters by direct reaction with
	Reason ·	Electron withdrawing groups
	Reason .	increase the acidity of phenols.
19.	Assertion	: <i>tert</i> -butyl alcohol undergoes acid
		catalysed dehydration readily than
		propanol.
	Reason :	3° alcohols do not give Victor-Meyer's
test.		
20.	Assertion	: The ease of dehydration of alcohols
		Secondary > Tertiary
	Reason :	Dehydration proceeds through the
		formation of oxonium ions.
21.	Assertion	: Phenol reacts with acyl halides in
		presence of pyridine to form phenyl
		acetate.
	Reason :	Benzoylation of phenol is carried out
		In the presence of NH_4OH .
22.	Assertion	: Alcohols are easily protonated than
	Deces	phenols.
	Reason :	Alconois undergo intermolecular
		of highly electronegative oxygen
23.	Assertion	: Phenol is less acidic than p-
0		nitrophenol.
	Reason :	Phenolate ion is more stable then <i>p</i> -
		nitrophenolate ion.
24.	Assertion	: Treatment of phenol with nitrous
		monovime
	Reason :	<i>p</i> -nitrosophenol and <i>p</i> -benzoquinone
		monoxime are tautomers.
25.	Assertion	: Reimer-Tiemann reaction of phenol
		with CCl_4 in NaOH at 340 K gives
		salicylic acis as the major product.
	Reason :	The reaction occurs through
		intermediate formation of
26	Accortion	alchlorocarbene.
20.	Assertion	he distinguished by Victor-Meyer's
		test.
	Reason :	Primary alcohols form nitrolic acid
		which dissolve in NaOH to form blood
		red colouration but secindary alcohols
		torm pseusonitrotes which give blue
27	Accertion	COLOURATION WITH NAUH.
2/.	79961 (1011	110_4 cleaves 1, 2-grycols but 10t 1,
	Reason .	3- or nigner givcols.
	Reason .	which subsequently undergo cleavage
		to form carbonyl compounds.
28.	Assertion	: Dehydration of glycerol with
		$KHSO_4$ gives acrolein.

Reason : Acrolein is an α , β -unsaturated aldehyde.

- 29. Assertion : Both symmetrical and unsymmetrical ethers can be prepared by Williamson's synthesis.
 Reason : Williamson's synthesis is an example
- of nucleophilic substitution reaction. **30.** Assertion : Etherates are coordination
- complexes of ethers with Lewis acids.
 Reason : Ethers are easily cleaved by mineral acids such as *HCl* and *H*₂*SO*₄ at 373 *K*.
- **31.** Assertion : $(CH_3)_3 Br$ and CH_3CH_2ONa react to form $(CH_3)_3C O CH_2CH_3$.
 - Reason : Good yields of ethers are obtained when tert-alkyl halides are treated with alkoxides.
- **32.** Assertion : A rate of hydrolysis of methyl chloride to methanol is higher in DMF than in water.
 - Reason : Hydrolysis of methyl chloride follows second order kinetics. [AIIMS 2005]
- **33.** Assertion : *t*-Butyl methyl ether is not prepared by the reaction of *t*-butyl bromide with sodium methoxide.

Reason: Sodium methoxide is a strong nucleophile.

[AIIMS 2005]



General introduction of alcohol, Phenol & Ethers

1	b	2	d	3	с	4	d	5	а
6	C	7	C	8	b	9	C	10	b
11	b	12	C	13	С	14	а	15	C
16	b	17	b	18	b	19	b	20	b
21	а	22	C	23	а	24	a	25	b
26	а	27	C	28	а	29	C	30	d
31	а	32	b	33	С	34	b	35	d
36	d	37	b	38	a	39	а		

Preparation of alcohol, Phenol and Ethers

1	c	2	с	3	b	4	c	5	d
6	C	7	C	8	d	9	а	10	b
11	C	12	C	13	b	14	b	15	d
16	C	17	b	18	С	19	d	20	b

21	C	22	b	23	С	24	C	25	C
26	d	27	а	28	d	29	b	30	а
31	b	32	b	33	d	34	C	35	d
36	С	37	a	38	а	39	b	40	C
41	b	42	а	43	а	44	C	45	C
46	b	47	C	48	b	49	а	50	b
51	d	52	a	53	d	54	a	55	C
56	a	57	b	58	С	59	b	60	bc
61	а	62	d	63	b	64	а		

Properties of alcohol, Phenol and Ethers

1	с	2	a	3	a	4	C	5	a
6	d	7	d	8	b	9	d	10	C
11	а	12	b	13	C	14	C	15	C
16	b	17	C	18	C	19	d	20	а
21	b	22	b	23	a	24	b	25	C
26	b	27	a	28	b	29	a	30	d
31	b	32	b	33	C	34	C	35	b
36	а	37	d	38	a	39	с	40	b
41	d	42	b	43	d	44	a	45	C
46	b	47	C	48	а	49	а	50	а
51	d	52	c	53	b	54	C	55	a
56	С	57	d	58	a	59	d	60	C
61	d	62	a	63	С	64	b	65	с
66	b	67	d	68	b	69	с	70	b
71	С	72	c	73	a	74	a	75	C
76	а	77	a	78	а	79	d	80	a
81	с	82	a	83	d	84	b	85	с
86	а	87	b	88	d	89	b	90	с
91	b	92	d	93	d	94	b	95	a
96	а	97	b	98	a	99	с	100	d
101	d	102	с	103	a	104	b	105	d
106	a	107	d	108	b	109	a	110	C
111	b	112	b	113	а	114	a	115	a
116	b	117	а	118	d	119	а	120	с
121	a	122	d	123	a	124	a	125	c
126	b	127	c	128	b	129	a	130	a
131	b	132	b	133	c	134	a	135	d
136	а	137	b	138	d	139	a	140	b
141	а	142	b	143	b	144	a	145	b

146 a 147 a 148 a 149 a 150 b 151 b 152 b 153 b 154 a 155 b 156 c 157 d 158 c 159 c 160 a 161 c 162 c 163 b 164 d 165 a 166 b 167 c 168 b 169 d 170 b 171 c 172 b 173 b 174 b 175 a 176 a 177 c 178 a 179 b 180 c 181 b 182 b 183 c 184 a 185 d 196 d 197 b 188 a 189 c 190 a 201 b 202 c 203 d 204 a 205 b 206 a										
151b152b153b154a155b156c157d158c159c160a161c162c163b164d165a166b167c168b169d170b171c172b173b174b175a176a177c178a179b180c181b182b183c184a185d186c187b188a189c190a191d192a193a194b195add196d197b198b199b200a201b202c203d204a205b206a207b218b214a215a211a212a213b214a215a226a227c228d229b230a231b232d233c234b235d236b237d238c239d240a	146	а	147	a	148	a	149	a	150	b
156c157d158c159c160a161c162c163b164d165a166b167c168b169d170b171c172b173b174b175a176a177c178a179b180c181b182b183c184a185d186c187b188a189c190a191d192a193a194b195add196d197b198b199b200a201b202c203d204a215b206a207b208b214a215a216c217d218d219a220a221b222a223d224b225c226a227c228d234b230a231b232d233c239d240a	151	b	152	b	153	b	154	a	155	b
161 c 162 c 163 b 164 d 165 a 166 b 167 c 168 b 169 d 170 b 171 c 172 b 173 b 174 b 175 a 176 a 177 c 178 a 179 b 180 c 181 b 182 b 183 c 184 a 185 d 186 c 187 b 188 a 189 c 190 a 191 d 192 a 193 a 194 b 195 add 191 d 192 a 193 a 194 b 195 add 191 d 192 a 203 d 204 a 205 b 201 b 202	156	С	157	d	158	c	159	С	160	а
166 b 167 c 168 b 169 d 170 b 171 c 172 b 173 b 174 b 175 a 176 a 177 c 178 a 179 b 180 c 181 b 182 b 183 c 184 a 185 d 186 c 187 b 188 a 189 c 190 a 196 d 192 a 193 a 194 b 195 add 196 d 197 b 198 b 199 b 200 a 201 b 202 c 203 d 204 a 205 b 201 b 202 c 203 d 204 a 205 b 206 a 207	161	С	162	С	163	b	164	d	165	а
171c172b173b174b175a176a177c178a179b180c181b182b183c184a185d186c187b188a189c190a191d192a193a194b195add196d197b198b199b200a201b202c203d204a205b206a207b208b209b210b211a212a213b214a215a226a227c228d229b230a231b232d233c234b235d236b237d238c239d240a	166	b	167	С	168	b	169	d	170	b
176a177c178a179b180c181b182b183c184a185d186c187b188a189c190a191d192a193a194b195add196d197b198b199b200a201b202c203d204a205b206a207b208b209b210b211a212a213b214a215a216c217d218d219a220a226a227c228d229b230a231b232d233c234b235d236b237d238c239d240a	171	c	172	b	173	b	174	b	175	а
181 b 182 b 183 c 184 a 185 d 186 c 187 b 188 a 189 c 190 a 191 d 192 a 193 a 194 b 195 add 191 d 192 a 193 a 194 b 195 add 196 d 197 b 198 b 199 b 200 a 201 b 202 c 203 d 204 a 205 b 206 a 207 b 208 b 209 b 210 b 211 a 212 a 213 b 214 a 215 a 216 c 217 d 218 d 224 b 225 c 226 a 227	176	а	177	С	178	а	179	b	180	C
186 c 187 b 188 a 189 c 190 a 191 d 192 a 193 a 194 b 195 add 196 d 197 b 198 b 199 b 200 a 201 b 202 c 203 d 204 a 205 b 206 a 207 b 208 b 209 b 210 b 211 a 212 a 213 b 214 a 215 a 211 a 212 a 213 b 214 a 215 a 216 c 217 d 218 d 219 a 220 a 2216 a 222 a 223 d 224 b 230 a 231 b 232	181	b	182	b	183	C	184	а	185	d
191 d 192 a 193 a 194 b 195 ad 196 d 197 b 198 b 199 b 200 a 201 b 202 c 203 d 204 a 205 b 206 a 207 b 208 b 209 b 210 b 216 a 207 b 208 b 209 b 210 b 216 a 207 b 208 b 209 b 210 b 211 a 212 a 213 b 214 a 215 a 216 c 217 d 218 d 219 a 220 a 221 b 222 a 228 d 229 b 230 a 231 b 232	186	C	187	b	188	а	189	С	190	а
196 d 197 b 198 b 199 b 200 a 201 b 202 c 203 d 204 a 205 b 206 a 207 b 208 b 209 b 210 b 206 a 207 b 208 b 209 b 210 b 211 a 212 a 213 b 214 a 215 a 216 c 217 d 218 d 219 a 220 a 2216 c 217 d 218 d 219 a 220 a 2216 b 222 a 223 d 224 b 230 a 226 a 227 c 228 d 234 b 235 d 236 b 237	191	d	192	a	193	а	194	b	195	ad
201 b 202 c 203 d 204 a 205 b 206 a 207 b 208 b 209 b 210 b 211 a 212 a 213 b 214 a 215 a 216 c 217 d 218 d 219 a 220 a 216 c 217 d 218 d 219 a 220 a 221 b 222 a 223 d 224 b 225 c 226 a 227 c 228 d 229 b 230 a 231 b 232 d 238 c 234 b 235 d 236 b 237 d 238 c 239 d 240 a	196	d	197	b	198	b	199	b	200	a
206a207b208b209b210b211a212a213b214a215a216c217d218d219a220a221b222a223d224b225c226a227c228d229b230a231b232d238c234b235d236b237d238c239d240a	201	b	202	С	203	d	204	a	205	b
211a212a213b214a215a216c217d218d219a220a221b222a223d224b225c226a227c228d229b230a231b232d233c234b235d236b237d238c239d240a	206	а	207	b	208	b	209	b	210	b
216 c 217 d 218 d 219 a 220 a 221 b 222 a 223 d 224 b 225 c 226 a 227 c 228 d 229 b 230 a 231 b 232 d 233 c 234 b 235 d 231 b 232 d 233 c 234 b 235 d 236 b 237 d 238 c 239 d 240 a	211	а	212	a	213	b	214	a	215	a
221 b 222 a 223 d 224 b 225 c 226 a 227 c 228 d 229 b 230 a 231 b 232 d 233 c 234 b 235 d 236 b 237 d 238 c 239 d 240 a	216	C	217	d	218	d	219	а	220	а
226 a 227 c 228 d 229 b 230 a 231 b 232 d 233 c 234 b 235 d 236 b 237 d 238 c 239 d 240 a	221	b	222	a	223	d	224	b	225	C
231 b 232 d 233 c 234 b 235 d 236 b 237 d 238 c 239 d 240 a	226	а	227	с	228	d	229	b	230	а
236 b 237 d 238 c 239 d 240 a	231	b	232	d	233	c	234	b	235	d
	236	b	237	d	238	c	239	d	240	а
241 a 242 a 243 b 244 a 245 a	241	а	242	а	243	b	244	а	245	a

Uses of alcohol, Phenol and Ethers

1	а	2	c	3	d	4	b	5	b
6	а	7	а	8	a	9	a	10	b
11	d	12	d	13	d	14	b	15	d
16	d	17	b	18	C	19	С	20	b
21	c	22	c	23	C	24	d	25	C
26	d	27	а	28	а				

Critical Thinking Questions

1	c	2	C	3	с	4	а	5	а
6	C	7	C	8	C	9	а	10	C
11	d	12	b	13	а	14	b	15	а
16	d	17	b	18	a	19	b	20	C
21	C	22	a						

Assertion & Reason

1	С	2	d	3	а	4	с	5	С
6	a	7	b	8	а	9	b	10	a
11	С	12	а	13	b	14	е	15	е

16	c	17	е	18	b	19	b	20	е
21	C	22	b	23	C	24	b	25	C
26	а	27	а	28	b	29	b	30	C
31	d	32	c	33	b				



General introduction of alcohol, Phenol & Ethers

2. (d)
$$O_2 N \xrightarrow{OH}_{NO_2} NO_2$$

2, 4, 6-trinitrophenol or picric acid

4. (d) $CH_2 - CH - CH_2$ Glycerol is trihydric alcohols. | | | | | OH OH OH

5. (a)
$$OH$$

Hydroxy

6. (c) % of
$$C = \frac{Mass of C}{Mass of substance} \times 100$$

 $CCl_4 = \frac{12}{154} \times 100 = 7.79 \%$
 $C_6H_6Cl_6 = \frac{72}{291} \times 100 = 24.74 \%$
 $CH_2OH - CH_2OH = \frac{24}{62} \times 100 = 38.70 \%$.
OH
7. (c) OH o-dihydroxy benzene or catechol.

8. (b) *CH*-*OH*

 $CH_2 - OH$

 $CH_2 - OH$

one secondary and two primary alcoholic groups.

- **11.** (b) Carbinol is CH_3OH (Methanol).
- **12.** (c) *OH* group is attached to primary carbon. *OH*

13. (c)
$$O_2N \longrightarrow NO_2$$

 NO_2

(Picric acid) or 2, 4, 6-

Picric acid is phenolic while others are non phenolic. **15.** (c) Butanal $CH_3 - CH_2 - CH_2 - CHO$, an aliphatic

aldehyde. *OH* Cyclohexanol is a secondary alcohol because -OH group is linked to 2° carbon.

- **18.** (b) C_2H_5OH and $CH_3 O CH_3$ are isomers.
- 20. (b) 5-10 % methyl and remaining ethanol is called methylated spirit. It is also known as denatured alcohol because it is unfit for drinking.



- **23.** (a) 5% aqueous solution of phenol at room temperature is called as carbolic acid.
- 25. (b) Glycols are dihydric alcohols (having two hydroxyl groups). Ethylene glycol is the first member of this series.
 CH₂OH
 CH₂OH
 CH₂OH

- 26. (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.
- 34. (b) Ether is basic because lone pairs of electrons are present on oxygen atom, R - O - R.
- **39.** (a) Thio alcohol is known as mercaptans.

Preparation of alcohol, Phenol and Ethers

1. (c) Hydration of alkenes

2.

4

$$CH_{2} = CH_{2} + HHSO_{4} \rightarrow CH_{3} - CH_{2} - HSO_{4}$$

$$CH_{3} - CH_{2}HSO_{4} \xrightarrow{H_{2}O} CH_{3} - CH_{2} - OH + H_{2}SO_{4}$$
Fermentation of sugars:
$$C_{12}H_{22}O_{11} + H_{2}O \xrightarrow{\text{Invertase}} C_{6}H_{12}O_{6} + C_{6}H_{12}O_{6}$$

$$C_{6}H_{12}O_{6} \xrightarrow{\text{Zymase}} 2C_{2}H_{5}OH + 2CO_{2}$$
Glucose or Fructose
$$C_{6}H_{12}O_{6} \xrightarrow{H_{2}O_{4}} CH_{3} - CH_{2} - CH_{2} + CO_{2}$$

$$C_{12}H_{22}O_{11} + H_{2}O \xrightarrow{\text{Invertase}} 2C_{2}H_{5}OH + 2CO_{2}$$

$$C_{12}H_{22}O_{11} + H_{2}O \xrightarrow{H_{2}O_{4}} CH_{2} + CO_{2}$$

$$C_{12}H_{22}O_{11} + H_{2}O \xrightarrow{H_{2}O_{4}} CH_{2} + CO_{2}$$

$$C_{12}H_{2}O_{6} \xrightarrow{H_{2}O_{4}} CH_{2} + CO_{2}$$

$$C_{12}H_{2}O_{4} + CO_{2}$$

$$C_{12}H_{2}O_{4} + CO_{2}O_{4} + CO_{2}O_{4} + CO_{2}O_{4} + CO_{2}O_{4} + CO_{2}O_{4} + CO_{4}O_{4} + CO_{4}O_{4$$

(c)
$$CH_2 = CH_2 \xrightarrow{H_2SO_4} CH_3 - CH_2 - HSO_4 \xrightarrow{\text{Hydrolysis}} CH_2CH_2 - OH + H_2SO_4$$

3. (b) Hydroboration oxidation (Industrial preparation of alcohol)

$$3CH_{3}CH = CH_{2} + \frac{1}{2}B_{2}H_{6} \xrightarrow{\text{Dry}} (CH_{3}CH_{2}CH_{3})_{3}B$$

$$(CH_{3}CH_{2}CH_{3})_{3}B \xrightarrow{H_{2}O_{2}} 3CH_{3}CH_{2}CH_{2} - OH$$

$$(c) \quad CH_{2} - CH_{2} + CH_{3}MgI \rightarrow CH_{2} - CH_{2} \rightarrow H_{2} \xrightarrow{H_{2}O_{2}} OH_{2}CH_{2} \xrightarrow{H_{2}O_{2}} OH_{2} O$$

16.

(b)

$$CH_3 - CH_2 - CH_2 - OH + Mg < I_{OH}$$

- 5. (d) Starch $\xrightarrow{\text{Enzymes}}$ Alcohol
- 6. (c) Coconut oil + Alkali \rightarrow Soap + Glycerol It is a saponification reaction.
- 7. (c) $C_6 H_{12} O_6 \xrightarrow{Zymase} 2C_2 H_5 OH + 2CO_2$ Glucose or Fructose Ethylalcohol

8. (d)
$$(d) \xrightarrow{CH_2}_{\text{Light/heat}} \xrightarrow{CH_2 CI}_{\text{Benzylchloride}} CH_2 - OH$$

 $\xrightarrow{aq.NaOH}_{\text{Benzylalcohol}} + NaCL$

9. (a) $2(C_6H_{10}O_5)_n + nH_2O_{(\text{from germinated barley})} n(C_{12}H_{22}O_{11})$ $C_{12}H_{22}O_{11} + H_2O_{(\text{from yeast})} 2C_6H_{12}O_6$ $C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$

10. (b)
$$N = N - Cl$$
 OH
11. (c) \rightarrow $+ H_2O \xrightarrow{\Lambda}$ \rightarrow \rightarrow $+ N_2 + HCl$

12. (c) $CH_3COOH + 4H \xrightarrow{LiAlH_4} CH_3CH_2OH + H_2O$

13. (b)
$$\stackrel{H}{H} C = O \xrightarrow{CH_3MgI} CH_2 - O - MgI \xrightarrow{Hydrolysis} CH_3$$

$$CH_3 - CH_2 - OH + Mg < I_{OH}$$



15. (d)
$$(D)$$
 (D) $(D$

16. (c)
$$C_2H_5ONa + IC_2H_5 \rightarrow C_2H_5OC_2H_5 + Nal$$

 OH
17. (b) OH
 $+ 3NaCl + 2H_2O$

18. (c) $HCHO + HCHO \xrightarrow{\text{Conc. KOH}} CH_3OH + HCOOK_{\text{Methyl alcohol}} + HCOOK_{\text{Potassium formate}}$ It is cannizzaro's reaction. **19.** (d) Alcohol + Benzene \rightarrow Soluble

(Alcohol) $R - OH + Na \rightarrow R - ONa + H_2$

21. (c)
$$\underbrace{CO + H_2}_{\text{water gas}} + H_2 \xrightarrow{Cr_2O_2/ZnO} CH_3OH$$



24. (c)
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[(from yeast)]{Maltose} 2C_6H_{12}O_6$$
.

- 26. (d) Grignard reagent reacts with compounds containing multiple bonds like >C=O, >C=S, >C=N.
- **28.** (d) Acetone reacts with Grignard's reagent to give tertiary alcohol.

$$(CH_3)_2 C = O + CH_3 MgBr \xrightarrow{H_2 O} (CH_3)_3 C - OH_{\text{ter-butyl alcohol}}$$

29. (b)
$$C_2H_5MgBr + H_2C - CH_2 \xrightarrow{H_2O} O$$

 $C_2H_5CH_2CH_2OH + MgBr(OH)$ (A) *n*-butyl alcohol

30. (a)
$$\xrightarrow{NaOH}_{H^+/H_2O}$$
 \xrightarrow{Phenol}

SO-Ma

31. (b)
$$N = N - Cl$$
 OH
 $H_2O \xrightarrow{\text{Boil}} OH + N_2 + HCl$
Phenol

32. (b)
$$\stackrel{H}{\to} C = O + C_2 H_5 MgI \rightarrow CH_2 - O - MgI$$

$$\xrightarrow{\text{Hydrolysis}} C_2H_5 - CH_2 - OH \text{ or } C_3H_7OH + Mg < \frac{I}{OH}$$

35. (d) $RMgBr + O_2 \rightarrow R - OMgBr \xrightarrow{hydrolysis} R - OH + Mg < {Br} \xrightarrow{Grignard} reagent$

39. (b)
$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

Glucose

During fermentation CO_2 gas is eliminated.

40. (c)
$$C_2H_5 - NH_2 + HNO_2 \rightarrow C_2H_5OH + N_2 + H_2O$$



 $CH_2 - OH$

Benzyldehyde

Benzyl alcohol

41. (b)

$$41. (b) \xrightarrow{LAHH_4}$$
42. (a) $CO + H_2 \xrightarrow{CuO - 2nO - Cr_2O_3}{573 K, 200 atm} \xrightarrow{CH_3OH} Methanol$
43. (a) $CH_3 - CH = C < \overset{CH_3}{CH_3} + H_2O \xrightarrow{H_2SO_4} Methanol$
43. (a) $CH_3 - CH = C < \overset{CH_3}{CH_3} + H_2O \xrightarrow{H_2SO_4} Methanol$
2 methyl butene
$$CH_3 - CH_2 - C < \overset{CH_3}{CH_3} + H_2O \xrightarrow{H_2SO_4} OH + 2 methyl buten-2 ol$$

$$OH \\ CH_3CH = CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3 - CH - CH_3 \\ propene - 2 - ol$$
44. (c) $CH_3CONa + Br - CH_3 \rightarrow CH_3 - O - CH_3 + NaBr \\ Dimethyl ether \\ (cymmetrial ether)$

$$CH_3 - \overset{CH_3}{C} - O^-Na + CH_3Br \rightarrow CH_3 - \overset{CH_3}{C} - OCH_3 + NaBr \\ CH_3 - \overset{CH_3}{C} - O^-Na + CH_3Br \rightarrow CH_3 - \overset{CH_3}{C} - OCH_3 + NaBr \\ CH_3 - \overset{CH_3}{C} - O^-Na + CH_3Br \rightarrow CH_3 - \overset{CH_3}{C} - OCH_3 + NaBr \\ CH_3 - \overset{CH_3}{C} - O^-R + NaX \\ Methyl lerberical ether)$$
45. (c) $\overset{OH}{\bigcirc} + RX \xrightarrow{Alkali} \overset{O}{\bigcirc} + HX$
46. (b) $C_2H_5Br + C_2H_5ONa \xrightarrow{-NaBr}{C} C_2H_5 - O - C_2H_5 \\ sod ethaoxide \xrightarrow{-NaBr}{C} C_2H_5 - O - C_2H_5 \\ Methyl ether \\ It is a Williamson's synthesis reaction.$
48. (b) Williamson's synthesis - $CH_3 - CH_2 - OH_3 \rightarrow CH_3 - CH_2 - O - CH_2 - CH_3 \rightarrow CH_3 - CH_2 - O - CH_3 - CH_3 \rightarrow CH_3 - CH_2 - O - CH_3 - CH_3 - CH_2 - O - CH_3 - CH_3 - CH$

If we take moist Ag_2O then alcohol is formed $Ag_2O + H_2O \rightarrow 2AgOH$

$$C_2H_5Br + AgOH \rightarrow C_2H_5OH + AgBr$$

51. (d)
$$CH_3OCH_3 \xrightarrow{Cl_2/h\nu} CH_3OCH_2Cl_{\alpha-Chlorodime thy lether$$

$$\underbrace{\xrightarrow{CH_3MgBr}_{-MgBr(Cl)}}_{\text{Methoxyethane}} \underbrace{CH_3OCH_2CH_3}_{\text{Methoxyethane}}_{\text{(Higher ether)}} 3$$
52. (a)
$$\underbrace{CH_3 - C - Br}_{\text{Acetyl bromide}} \underbrace{CH_3 - C - OH}_{\text{(ii) Saturated } NH_4Cl} CH_3 - \underbrace{CH_3 - C - OH}_{CH_3}_{2-\text{methyl 2-propanol}}$$

(d) When chlorine is passed in boiling toluene, 53. substitution inside chain takes place and benzyl chloride is obtained which on hydchlysis give bentzol alcohol. CH2OH



- 54. (a) $2C_6H_5CHO + NaOH \rightarrow C_6H_5CH_2OH + C_6H_5COONa$ Benzaldehy de (Benzylalcohol)
- (c) Ethanal with CH_3MgBr gives propanol-2 55. (after hydrolysis) and with C_2H_5OH , it gives acetal.

$$\xrightarrow{[NaHCO_3]} H_2C - CH_2 + NaCl + CO_2$$

$$\xrightarrow{|} OH OH$$
(Ethy lene gly col)

57. (b)
$$CH_3 \xrightarrow{I}_{-C-O-Na+Cl-CH_3} \rightarrow CH_3$$

 CH_3
 $2, 2 \text{ dimethyl sodium ethoxide}$

0

$$CH_{3}$$

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

$$CH_{3}$$

$$CH_{3}$$
Methyl-t butyl ether
$$O - MeI$$

58. (c)
$$CH_3 - C - OC_2H_5 + CH_3MgI \rightarrow CH_3 - C - OC_2H_5$$

Ethylmethylester $CH_3 - C - OC_2H_5$

$$\xrightarrow{Hy \text{ droly sis}} CH_3 \xrightarrow{C} CH_3 \xrightarrow{C} OC_2H_5 \xrightarrow{+M_g < OH} CH_3 \xrightarrow{CH_3 < C} OC_2H_5 \xrightarrow{+M_g < OH} CH_3 \xrightarrow{CH_3 < C} OC_2H_5 \xrightarrow{C} OC_2$$

59. (b) $NaBH_4$ and $LiAlH_4$ attacks only carbonyl group and reduce it into alcohol group. They do not attack on double bond.

$$C_{6}H_{5} - CH = CHCHO \xrightarrow{NaBH_{4}}$$

cinnamic aldehy de
$$C_{4}H_{4} - CH = CH$$

$$C_6H_5 - CH = CH.CH_2OH$$

cinnamic alcohol

60. (b,c)

$$CH_{2} = CH_{2} + H_{2}O + [O] \xrightarrow{\text{alk.KMnO}_{4}} CH_{2} - CH_{2}$$
$$| \\ OH OH$$
$$Glycol$$



Properties of alcohol, Phenol and Ethers

1. (c) $CH_3 - OH + CH_3 Mg - X \rightarrow CH_4 + CH_3 O - Mg - X$ 4. (c) $C_2H_5OH \xrightarrow{NaOH/I_2} CHI_3$ (yellow ppt)

$$CH_{3}OH \xrightarrow{NaOH / I_{2}} \text{No } ppt$$
5. (a)
$$CH_{3} - CH_{2} - CH_{2} - OH \xrightarrow{Oxidation} CH_{3}CH_{2}COOH$$

Since on oxidation same no. of carbon atoms are obtained in as therefore alcohol is primary

8. (b)
$$+$$

 $+ 3KC(A) 3H_2O$ $N \equiv C$
 $3KOH + CHCl_3 \rightarrow$

$$C_{2}H_{5}OH + Cl_{2} \xrightarrow{Ca(OH)_{2}} CH_{3}CHO \xrightarrow{Cl_{2}} Accetaldehyde} CCl_{3}CHO \xrightarrow{Cd(OH)_{2}} CHCl_{3} CHOl_{3} Chloral \xrightarrow{Chloroform} (Y)$$

$$I2. (b) \xrightarrow{OH} \xrightarrow{Conc. HNO_{3}} \underbrace{NO_{2} \xrightarrow{OH} NO_{2}}_{(Conc. H_{2}SO_{4}} \underbrace{OH} \xrightarrow{OH} \underbrace{OH} \underbrace{O$$

$$\begin{array}{c} \xrightarrow{H^{+}} & & & & & & & & & & & & & & \\ \xrightarrow{P-\text{Aminoazobe nzene (yellowppt.)}} \\ \textbf{16.} \quad (b) \quad \stackrel{CH_2 - OH}{\underset{I}{CH - OH}} \stackrel{CH_2 - I}{\underset{Small amount}{H^{-1} - I}} \stackrel{CH_2 - I}{\underset{I}{CH_2 - I}} \stackrel{CH_2 - I}{\underset{CH_2 - I}{CH_2 - I}} \\ \textbf{18.} \quad (c) \quad \stackrel{CH_2 - OH}{\underset{I}{CH - OH}} \stackrel{3HI}{\underset{-3H_2 O}{H^{-1} - I}} \stackrel{CH_1 - I}{\underset{I}{CH - I}} \stackrel{-I_2}{\underset{-I_2}{-I_2}} \\ \textbf{18.} \quad (c) \quad \stackrel{CH_2 - OH}{\underset{I}{CH - OH}} \stackrel{CH_2 - I}{\underset{-3H_2 O}{H^{-1} - I}} \\ \textbf{18.} \quad (c) \quad \stackrel{CH_2 - OH}{\underset{I}{CH - OH}} \stackrel{CH_2 - I}{\underset{-3H_2 O}{H^{-1} - I}} \\ \textbf{18.} \quad (c) \quad \stackrel{CH_2 - OH}{\underset{I}{CH - OH}} \stackrel{CH_2 - I}{\underset{-3H_2 O}{H^{-1} - I}} \\ \textbf{19.} \quad (d) \quad HOOC - COOH \stackrel{Glycerol}{\underset{I}{Glycerol}} HCOOH + CO_2 \\ \end{array}$$

9. (d)
$$HOOC - COOH \xrightarrow{P}_{\text{Decarboxy hion}} HCOOH + CO_2$$

 $HCOOH + \text{Fehling solution} \rightarrow Cu_2O + CO_2 + H_2O$
Red ppt.

21. (b) Glycerol undergoes extensive hydrogen bonding due to the presence of 3 - OH groups. As a result the glycerol molecules are highly associated and thus it has high viscosity. $CH_2 - OH$ CH_2

22. (b)
$$\begin{array}{c} \stackrel{|}{C}H^{-}OH & \xrightarrow{\text{conc.}} \\ \stackrel{|}{H_{2}SO_{4}} & \stackrel{|}{C}H^{-} + 2H_{2}O \\ CH_{2} - OH & CHO \\ Acrolein \end{array}$$

23. (a) $CH_{3} - CH - CH_{3} \xrightarrow{\text{Oxidation}} CH_{3} - CH_{3} + CH_{3$

23. (a)
$$CH_3 - CH - CH_3 \xrightarrow{KMnO_4} CH_3 - C - CH_3$$

 $| OH OH OAcetone$

24. (b)
$$\bigcirc$$
 $N = Cl + H \bigcirc$ $OH \xrightarrow{OH^-}$ $H \xrightarrow{OH^-}$ $N = \bigcirc$ OH \longrightarrow P -hydroxyazobenzene

25. (c)
$$(CH_3)_3 C - OH + HCl \xrightarrow{Anhyd. ZnCl_2 + HCl}$$

 $(CH_3)_3 C - Cl + H_2O \quad 3^o \text{ reacts immediately}$
 $(CH_3)_3 CH - OH + HCl \xrightarrow{Anhyd. ZnCl_2 + HCl}$
 $(CH_3)_2 CH - Cl + H_2O \quad 2^o \text{ reacts after 5 min.}$
 $CH_3CH_2CH_2 - OH + HCl \xrightarrow{Anhyd. ZnCl_2 + HCl}$
 $CH_3CH_2CH_2 - Cl + H_2O \quad 1^o \text{ reacts only on}$

heating.
26. (b)
$$C_2H_5OH + R - Mg - X \rightarrow RH + C_2H_5OMgX$$

 $C_3H_7OH + R - Mg - X \rightarrow RH + C_3H_7OMgX$
30. (d) $H \rightarrow OH$
 H

OH OH Phenolphthale

~...

50. (a)

$$CH_2OH$$
33. (c) | + HIO₄ \rightarrow 2HCHO + HIO₃ + H₂O
CH₂OH

35. (b)
$$CH_2OH \\ \vdash \\ CH_2OH \\ CH_2I \\ CH_2I \\ CH_2I \\ CH_2 = CH_2$$

39. (c)

(a)

$$R - OH + (NH_4)_2 Ce(NO_3)_6 \rightarrow Ce(NO_3)_6 (ROH)_9 + 2N + 14 NO_3$$

alcohol Cerric amm. nitrate yellow ppt.

37. (d)
$$C_2H_5 - O - C_2H_5 + O_2 \xrightarrow{hv}_{25^{\circ}C} CH_3 - CH(OOH) - O - C_2H_5$$

38. (a)
$$H_2SO_4 \to H^+ + HSO_4^-$$

$$C_{2}H_{5}OH + H^{+} \xrightarrow{\text{Protonatio n}} C_{2}H_{5} - \overset{\bigoplus}{O-H}$$

$$H$$

$$OH \qquad OH \qquad Protonated alcohol$$

$$M = NO \qquad Nitro group is electron$$

*O*² with-drawing. Hence, increases acidic < [0]

43. (d)
$$CH_3CH_2OH \xrightarrow[(X)]{Al_2CO_3} CH_2 = CH_2 + H_2O$$

44. (a)
$$\bigcirc \xrightarrow{CO_2,400K} 3-7 \text{ atm} \bigcirc \xrightarrow{OCO_2Na} OH$$

45. (c)
$$C_2H_5OH \xrightarrow{H_2SO_4} C_2H_5HSO_4 + H_2O$$

 $137^{\circ}C \xrightarrow{C_2H_5 - O - C_2H_5 + H_2O}$
 $170^{\circ}C \xrightarrow{C_2H_4 + H_2O}$
Ethene

46. (b)
$$CH_3 - CH_3 - CH_3 - CH_3 - CH_3 - CH_3 + CH_3 CH_2 > CH_3 - CH_3 CH_2 - CH_3 CH_3 - CH_3 -$$

(c) Alcohols having less number of carbon atoms 47. are more soluble in water.

48. (a)
$$C_2H_5OH + Na \rightarrow C_2H_5ONa$$

$$2C_{2}H_{5}OH \xrightarrow{\text{Conc.}} C_{2}H_{5} - O - C_{2}H_{5} + H_{2}O$$

$$\xrightarrow{I}_{H_{2}SO_{4}} Cl \qquad Cl \qquad Cl$$

$$\xrightarrow{I}_{H_{2}SO_{4}} CH_{3} - CH - O - CH - CH_{3}$$

$$\xrightarrow{\alpha - \alpha' - \text{dichlorodiethyl}} \alpha - \alpha' - \text{dichlorodiethyl}$$

$$\xrightarrow{\text{other}} CCl_{3} - CCl_{2} - O - CCl_{2} - CCl_{3}$$

< 1x

51. (d)
$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$$

(A) (B)
 $C_2H_5Cl + KCN \rightarrow C_2H_5CN + KCl$
(B)
 $C_2H_5 - COOH$
52. (c) OH OH OH OH
 CH_3 OH OH OH
 OH OH OH
 OH OH

- 53. (b) Higher alcohols are stronger and have bitter taste.
- 54. (c) Order of reactivity with alkali metal (e.g.-Sodium) follows the order $1^{\circ} > 2^{\circ} > 3^{\circ}$.

56. (c)
$$CH_3OH + Na \rightarrow CH_3ONa + \frac{1}{2}H_2$$

 $1mole$ $1mole$
 $(23\,gms)$ $1/2mole$

57. (d)
$$3CH_3CH_2CH_2CH_2 - OH + PBr_3 \rightarrow$$

 $3CH_3CH_2CH_2CH_2 - Br + H_3PO_3$

58. (a)
$$CH_3OH + Cl_2 \rightarrow No$$
 reaction
 $CH_3OH + HCl \xrightarrow{Z_1Cl_2} CH_3Cl + H_2O$
 $3CH_3OH + PCl_3 \rightarrow 3CH_3Cl + H_3PO_3$
 $CH_3OH + PCl_5 \rightarrow CH_3Cl + POCl_3 + HCl$

59. (d)
$$CH_3 - CH - CH_3 \xrightarrow{[O]} CH_3 - C - CH_3$$

 $OH OH O$

60. (c)
$$OH$$

Phenol Br
 B

61. (d) Due to hydrogen bonding.

62. (a)
$$C_2H_5OH \xrightarrow{P_t} CH_3CHO$$

63. (c)
$$CH_3 - CH_2 - OH \xrightarrow{\text{Conc. } H_2SO_4} CH_2 = CH_2 + H_2O$$

66. (b) Tertiary alcohol readily reacts with halogen acid

$$\begin{array}{ccc} CH_3 & CH_3 \\ \downarrow & & | \\ CH_3 \rightarrow C - OH \rightarrow CH_3 - C^+ + OH \\ \uparrow & & | \\ CH_3 & CH_3 \end{array}$$

Presence of 3 alkyl group increases electron density on 3° carbon atom. Hence -OH group is easily removed. After the removal of -OH group 3° carbonium ion is formed which is most stable

- **67.** (d) $CH_3CH_2CH_2OH \xrightarrow{\text{conc. } H_2SO_4} CH_3CH = CH_2$ $\xrightarrow{Br_2} CH_3 - CH - CH_2 \xrightarrow{\text{Alc. } KOH} CH_3 - C \equiv CH_3 - C \equiv CH_3$ Br Br Br
- **68.** (b) Lower alcohols are soluble in all solvents.

69. (c)
$$CH_3 - CH - CH_2 - CH_3 \xrightarrow{[O]} CH_3 - \overset{O}{C} - CH_2CH_3$$

70. (b) Due to the resonance stabilisation of phenoxide ion.

73. (a)
$$R - CH_2 - CH_2 - OH \xrightarrow{\text{Conc. } H_2SO_4}{170 \, {}^{o}C}$$

 $R - CH = CH_2 + H_2O$
Alkene

74. (a)
$$R - CH_2OH \xrightarrow{Cu} R - CHO + H_2$$

 $1^{\circ} \text{ alcohol}$
 $R - CH - R \xrightarrow{Cu} R - C - R + H_2$
 OH
 $2^{\circ} \text{ alcohol}$

75. (c)
$$CH_3OH \xrightarrow{K_2Cr_2O_7} HCOOH_{H_2SO_4}$$

76. (a)
$$CH_3CH_2OH \xrightarrow{K_2Cr_2O_7} CH_3COOH$$

77. (a) Lucas test is used for the distinction of primary secondary and tertiary alcohols.

78. (a)
$$OH$$
 $H_3 \xrightarrow{ZnCl_2} O$ H_2 H_2O

- 80. (a) A compound that undergoes bromination easily is phenol. Due to presence of OH group the ring becomes much more active in substitution reactions. The bromination occurs due to availability of electrons on ortho and para position.
- **81.** (c) *o*-Nitrophenol has intramolecular *H*-bonding.
- **84.** (b) C_2H_5OH gives iodoform test having α -hydrogen atom while CH_3OH does not give due to the absence of α -hydrogen atom.
- **85.** (c) Phenol has higher boiling point than toluene because of hydrogen bonding.
- **87.** (b) $CH_3 CH = CH_2 + aq. KOH \rightarrow CH_3 CH_2 CH_2OH$ Propene -1 Propanol -1

88. (d)
$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl \xrightarrow{KCN} C_2H_5CN$$

 $\downarrow HCl / H_2O$
 C_6H_5COOH

89. (b) $LiAlH_4$ + ether, is reducing agent.



Oxygen atom of -OH group acquires positive charge.



OН

101. (d)

102. (c) Phenol is weaker acid than carbonic acid

In presence of non-polar solvent (CS_2) the ionization of phenol is suppressed. The ring is slightly activated and hence mono substitution occurs.

On the other hand with Br_2 water phenol forms 2,4,6-tribromo phenol.



$$+ 3Br_2 \xrightarrow{\text{water}} + 3HBr$$

In aqueous solution phenol ionizes to give phenoxide ion. Due to the presence of negative charge on oxygen the benzene ring is highly activated and hence trisubstituted product is obtained.

105. (d)
$$C_{2}H_{5}OH \xrightarrow{C\partial O} CH_{3}COOH$$

Ethylalcohol Aceticacid
107. (d) $C_{2}H_{5}OH \xrightarrow{Conc.H_{2}SO_{4}} C_{2}H_{4} + H_{2}O$
Ethanol $\delta^{-} \delta^{+} \delta^{-} \delta^{+} \delta^{-} \delta^{+}$
 $O-H \cdots O-H$
108. (b) $OH \qquad O^{-}$
 $H = OH \qquad O^{-}$
109. (a) $OH \qquad O^{-} + H^{+}$
Phenol Phenoxide

110. (c) (a) $CH_3 - CH - CH_3 \xrightarrow{\text{Oxidation}} CH_3 - C - CH_3$ $OH \qquad O$ (b) $CH_3 - CH_2 - OH \xrightarrow{\text{Conc.} H_2SO_4}{180°C} CH_2 = CH_2 + H_2O$

(d)
$$2CH_3CH_2OH + 2Na \rightarrow 2CH_3 - CH_2 - ONa + H_2$$

- **112.** (b) Carbylamine reaction $CHCl_3 + CH_3NH_2 + 3KOH \rightarrow CH_3N \equiv C + 3KCl + 3H_2O$ Methyl isocyanide
- **113.** (a) Secondary alcohol on dehydrogenation gives acetone

114. (a) $CH_3 - CH - CH_3 \xrightarrow{[o]} CH_3 - CH_3 - CH_3$ OH O

118. (d)
$$C_2H_5OH + [O] \rightarrow CH_3CHO \rightarrow CH_3COOH$$

Phenol



Br

2, 4, 6-tribromophenol

(ii)
$$+ 3Br_2 \longrightarrow + 3HBr$$

In *aq*. solution phenol ionize to give phenoxide in which highly activates benzene ring and give trisubstituted product while in presence of CS_2 an inert solvent phenol is unable to ionize due to which benzene ring is slightly activated. Hence, monosubstituted product is obtained.

122. (d) Traces of water from ethanol is removed by reacting with *Mg* metal.

123. (a)
$$\begin{array}{c} CH_2 - OH \\ | \\ CH - OH \\ | \\ CH_2 - OH \\ Gly cerol \end{array}$$
 $\begin{array}{c} COOH \\ - \\ COOH \end{array}$ $\begin{array}{c} 260^{\,o}C \\ - \\ COOH \end{array}$ $\begin{array}{c} CH_2 = CH - CH_2 - OH \\ - \\ Ally kalcohol \end{array}$

125. (c)
$$C_2H_5OH$$

 Al_2O_3
 $250 \circ C$
 $C_2H_5OC_2H_5 + H_2O$
Diethyl ether
 Al_2O_3
 $250 \circ C$
 $C_2H_4 + H_2O$
Ethene

126. (b)
$$CH_3 - CH - OH \xrightarrow{NaOH}_{I_2} CHI_3$$

1-phenyl ethanol

Iodoform test is given by compounds in which $CH_3 - CH -$ or $CH_3 - CH -$ group is present.

$$127. (c) \bigcirc H & O \\ + 3Br_2 & \longrightarrow \bigcirc H \\ Br & Br \\ Br & Br$$

1 mole 3 moles 1 mole

94 grams of phenol reacts with 480 gms. of Br_2 .

2 gm. of phenol
$$-\frac{480}{94} \times 2 = 10.22 \, gms.$$

128. (b) $2C_2H_5OH + 2Na \rightarrow 2C_2H_5ONa + H_2$

130. (a)
$$CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O$$

Esterification

131. (b) CH_3OH has highest boiling point because of hydrogen bonding.

132. (b)
$$H - C < 0 - H - 0 > C - H$$

Formic acid forms dimer due to which strangth of H-bond increases Hence, boiling point increases.

- **133.** (c) Lower members are soluble in water and solubility decreases with increasing molecular mass because hydrophobic character increases.
- **135.** (d) Alcohols can not be dried using anhydrous $CaCl_2$ because it forms an addition compound $CaCl_2.4CH_3OH$.

 CH_3

137. (b) Presence of methyl group increases electron density at *o*- and *p*- positions. Hence, it undergoes nitration readily.



150. (b)
$$CH_3CH_2 - OH + HO - CH_2 - CH_3 \xrightarrow{Conc. H_2SO_4}_{140^{\circ}C}$$

 $CH_3CH_2 - O - CH_2 - CH_3 + H_2O$
Diethyl ether
 $CH_3CH_2 - O - CH_2 - CH_3 + H_2O$
Diethyl ether
 $H = 0 - H = 0 - H$
151. (b) $H = 0 - H = 0 - H$
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Rate of electrophillic substitution reaction in phenol is faster than in benzene because presence of -OH group increases electron density at *o*- and *p*- positions.



155. (b) Secondary alcohol on dehydrogenation gives acetone

$$CH_{3} - CH - CH_{3} \xrightarrow{Cu}_{300^{0}C} CH_{3} - C - CH_{3} + H_{2}$$

$$OH \qquad O$$
156. (c) $C_{2}H_{5}OH \xrightarrow{NaOH/I_{2}} CHI_{3}$

$$CH_{3}COCH_{3} \xrightarrow{NaOH/I_{2}} CHI_{3}$$

$$CH_{3}OH \xrightarrow{NaOH/I_{2}} No \text{ reaction.}$$

157. (d) 2,4,6 Trinitro toulene (TNT) *Cl*



159. (c)
$$\begin{array}{c} CH_2 - OH \\ CH_2 - OH \\ CH - OH + 3HNO_3 \\ H_2SO_4 \\ CH_2 - OH \\ CH_2 - OH \\ CH_2 - OH \\ CH_2 - OH \\ COOH \\ H_2SO_4 \\ H_2SO_4 \\ H_2SO_4 \\ H_2SO_4 \\ CH_2 - ONO_2 \\ CH_2 - OH \\ CH_2 - OH \\ CH_2 - O - CO - CO - COOH \\ CH_2 - OH \\ COOH \\ H_2OH \\ COOH \\ H_2OH \\ CH_2 - OH \\ CH_2 - O$$

163. (b)
$$C_2H_5OH + CH_3COOH \xrightarrow{H_2SO_4}_{\text{Esterification}} CH_3COOC_2H_5 + H_2O_{\text{Ethylacetate}}$$

165. (a)
$$H$$
 + Zn $\xrightarrow{\text{Distillation}}$ OH + ZnO .
166. (b) Hydrogen bonding : $\begin{array}{c} \delta^{-} & \delta^{+} & \delta^{-} & \delta^{+} \\ 0 - H & \cdots & 0 - H \\ R & H & R \\ Alcohol & Water & Alcohol \end{array}$

167. (c)
$$HO + OH \xrightarrow{\text{Furning}} HO + OH \xrightarrow{\text{Furning}} H_2SO_4$$

 $HO + OH \xrightarrow{\text{Furning}} H_2SO_4$
 $CH_2 - CH_2$
 $Ethy lene glycol$
 $O + 2H_2O$

168. (b) Tertiary carbonium ion is the most stable and it will be given by dehydration of tertiary alcohol.

169. (d)
$$CH_3CH_2OH \xrightarrow{\text{Heterolytic}} CH_3CH_2O^- + H^+$$

- 170. (b) C_2H_5OH is soluble in water due to Hbonding.
- 173. (b) When ethanol dissolves in water then emission of heat and contraction in volume.
- 175. (a) Azeotropic distillation method -Rectified spirit + Benzene + water \downarrow Fractional distillation
 - First fraction at 331.8 *K* is ternary azeotrope $(H_2O 7.4\% + \text{Benzene } 74\% + \text{alcohol } 18.5\%)$
 - Second fraction 341.2 K is a binary azeotrope (Benzene 67.7% + Alcohol 32.2%)

Last fraction at 351*K* is absolute alcohol. ·----р

176. (a)
$$CH_3 - O - H + C_2H_5 MgBr \rightarrow C_2H_6 + Mg OCH_3$$

Methyl alcohol Ethyl magnesium Ethane
 $OH O - CH_3$

177. (c)
$$+ CH_2N_2 \xrightarrow{HBF_4} + N_2$$

180. (c) Alcohol is soluble in water due to *H*-bonding

183. (c) $CH_3CH_2 - OH + 2Cl_2 \rightarrow CCl_3 - CHO$

Oxidation will occur with chlorination of methyl group.

185. (d)
$$CH_{3}CHO \xrightarrow{NaOHI_{2}} CHI_{3}$$

 $CH_{3}CH_{2}OH \xrightarrow{NaOH/I_{2}} CHI_{3}$
 $CH_{3} - CH - CH_{3} \xrightarrow{NaOH/I_{2}} CHI_{3}$
 OH
Yellow ppt.

$$C_6H_5 - CH_2 - OH \xrightarrow{\text{NaOH}/I_2} \text{No yellow } ppt.$$

186. (c) Benzyl alcohol and cyclohexanol are not acidic while phenol and *m*-chlorophenol are acidic due to presence of electron withdrawing groups like $-NO_2$, -Cl, -CN increases the acidic character of phenols. Hence, mchlorophenol is more acidic than phenol.

187. (b) Three, these are

 $CH_3CH_2OCH_2CH_3$ (I), $CH_3OCH_2CH_2CH_3$ (II) and $CH_3OCH(CH_3)_2$ (III). Here I and II, I and III are pairs of metamers.

189. (c) CH_3OCH_3 and $C_2H_5OCH_3$ are gases while $C_2H_5OC_2H_5$ (b.p. 308 *K*) is low boiling liquid.

 ΩU

190. (a)
$$C_2H_5OC_2H_5 \xrightarrow{\text{Red }P/HI} 2C_2H_5I \xrightarrow{\text{Red }P/HI} 2C_2H_6I \xrightarrow{\text$$

191. (d)
$$C_2H_5OC_2H_5 + O_2 \rightarrow CH_3 - CH - O - C_2H_5$$

$$O - OH$$

Ether peroxide

192. (a)
$$C_2H_5OC_2H_5 + HI \rightarrow C_2H_5OH + C_2H_5I$$

 $O - C_2H_5 \qquad OH$

193. (a)
$$+ HBr - + C_2H_5Br$$

196. (d) $R - C = O + R'OH \xrightarrow{Dry HCl} + C_2H_5Br$
 H Dry HCl $R'OH$
 $R'OH$
 $R'OH$
 $R'OH$
 $R'OH$

198. (b) $CH_3 - O - CH_3 + 2HI \rightarrow 2CH_3I + H_2O$

199. (b) Only alkyl aryl ethers *e.g.*, $C_6H_5OCH_3$ undergoes electrophilic substitution reactions. 200. (a) $CH_{2}COCl + C_{2}H_{2}O - C_{2}H_{2} \rightarrow No$ reaction

200. (a)
$$CH_3COCI + C_2H_5O = C_2H_5 \rightarrow RO$$
 lead
201. (b) $\rightarrow HI \xrightarrow{Heat} OH + CH_3I$
202. (c) $R - O - R \xrightarrow{BF_3} R \xrightarrow{R} O: \rightarrow BF_3$
Etherate

011

- 203. (d) Due to inter-molecular hydrogen bonding in alcohols boiling point of alcohols is much higher than ether.
- **205.** (b) $CH_3 OCH_3$ does not have replaceable H – atom.

206. (a)
$$CH_3 - C - O - CH_3 + H_2 \rightarrow CH_3I + (CH_3)_3COH$$

207. (b)
$$CH_3CH(OH)CH_2CH_3 \xrightarrow{Conc. H_2SO_4} CH_3CH = CHCH_3$$

 $CH_3CH = CHCH_3$

$$CH_{3}CHOHCH_{2}CH_{3} \xrightarrow{[O]} CH_{3}COCH_{2}CH_{3}$$

Butanone

Butanone gives both an oxime and positive iodoform test, therefore, the original compound is 2-butanol.

208. (b)
$$CH_2OH + 2PCl_5 \rightarrow CH_2Cl + 2POCl_3 + 2HCl$$

 $CH_2OH CH_2Cl$
Ethylene glycol 1, 2 dichloroethane

- **209.** (b) C_2H_5OH (ethanol) is a very weak acid hence it does not react with *NaOH*. However it reacts with metallic sodium.
- **210.** (b) Methanol has high boiling point than methyl thiol because there us intermolecular hydrogen bonding in methanol and no hydrogen bonding in methyl thiol.

211. (a)
$$\begin{array}{c} CH_2OH \\ CHOH \\ CHOH \\ CH_2OH \\ Glycerol \end{array} \xrightarrow{(H_2-O-C-C-OH)}{(H_2OH)} \xrightarrow{(H_2-O-C-C-OH)}{(H_2OH)} \xrightarrow{(H_2OH)}{(H_2OH)} \xrightarrow{(H_2-O-C-H)}{(H_2OH)} \xrightarrow{(H_2-O-C-H)}{(H_2-O-C-H)} \xrightarrow{(H_2-O-C-H)}{(H_2OH)} \xrightarrow{(H_2-O-C-H)}{(H_2OH)} \xrightarrow{(H_2OH)}{(H_2OH)} \xrightarrow{(H_2OH)}{(H_2OH)}$$

- **212.** (a) Formation of a yellow precipitate on heating a compound with an alkaline solution of iodine is known as iodoform reaction. Methyl alcohol does not respond to this test. Iodoform test is exhibited by ethyl alcohol, acetaldehyde, acetone, methyl ketone and those alcohols which possess $CH_3CH(OH)$ group.
- **213.** (b) In friedal craft acylation, aromatic compounds such as benzene, phenol etc. undergo acylation with CH_3COCl in the presence of anhydrous $AlCl_3$ and gives ortho and para derivatives. Intermediate is $CH_{\beta}H^+ = O$ (acylium ion) of the reaction.



In fact denotes friedel craft alkylation.

214. (a) This reaction is known as Reimer Tiemann reactio ΩH



215. (a)
$$\begin{array}{c} COOH \\ | \\ COOH \\ | \\ COOH \\ oxalic acid \end{array} + \begin{array}{c} CH_2OH \\ CH_2OH \\ Gly cerol \end{array} \rightarrow \begin{array}{c} HCOOH \\ Formic acid \\ H_2OH \\ Gly cerol \end{array} \rightarrow \begin{array}{c} HCOOH \\ Formic acid \\ H_2OH \\ CH_2OH \\ C$$

Thus at 530 K allyl alcohol is formed.

216. (c)
$$\stackrel{CH_2OH}{|} \xrightarrow{\text{anh.} ZnCb} \xrightarrow{CH_3CHO} CH_3CHO$$

 $CH_2OH \xrightarrow{-H_2O} \xrightarrow{CH_3CHO} Acetaldehyde$

217. (d) Ethyl alcohol give positive iodoform test (*i.e.* yellow ppt. with *I*₂ and *NaOH*)

$$CH_{3}CH_{2}OH + 4I_{2} + 6NaOH \rightarrow$$

 $CHI_{3} + 5NaI + CH_{3}COONa + 3H_{2}O$
vellowppt.

- **218.** (d) Tertiary alcohols react fastest with hydrogen halides 2 methyl propan-2-ol is a tertiary alcohol.
- **219.** (a) When benzoic acid reacts with ethyl alcohol in the presence of sulphuric acid ethyl benzoate is formed. This is known as esterification.

$$C_{6}H_{5}COOH + C_{2}H_{5}OH \xrightarrow{H_{2}SO_{4}} C_{6}H_{5}COOC_{2}H_{5} + H_{2}O$$

$$C_{6}H_{5}COOC_{2}H_{5} + H_{2}O$$

$$Ethyl benzoate$$

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

$$Phenyl magnesium br omide$$

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

- **221.** (b) $Mg + CH_3I \xrightarrow{\text{Dryether}} CH_3MgI$
- **222.** (a) Ethyl alcohol on dehydration with conc. H_2SO_4 at 170°C gives ethylene

$$CH_{3}CH_{2}OH \xrightarrow[conc.H_2SO_4]{170°C} CH_{2} = CH_{2} + H_{2}O$$

Ethylalcohol $CH_{2}SO_{4}$ Ethylene
OH

223. (d)
$$CH_3 - CH_2 - CH - CH_3 \xrightarrow{\text{Dehydration}} CH_3 - CH_2 - CH = CH_2 + CH_3 - CH = CH - CH_3$$

l butene (Major product) l butene

224. (b) Fats are esters of higher fatty acids with glycerol, hence on alkaline hydrolysis they give back glycerol and sodium or potassium salt of acid (this is called soap). $CH_{2}OCOR \qquad CH_{2}OH$ $\stackrel{|}{CHOCOR + 3NaOH \rightarrow CHOH + 3RCOONa$ $CH_{2}OCOR \qquad CH_{2}OH$ Fat **225.** (c) $CH_{3} - \stackrel{|}{C} - CH_{3} \xrightarrow{Cu}{300^{0}C} CH_{3} - C = \stackrel{|}{C}H_{2} + H_{2}O$ $CH_{3} \xrightarrow{CH_{3}} CH_{3} - C = \stackrel{|}{C}H_{2} + H_{2}O$

227. (c)
$$CH_3 - C \leftarrow OH \qquad OH \qquad H_3 - C - OH + H_2O$$

If two or more -OH groups are present on carbon atom then it immediately looses water molecule and forms acid or aldehyde.

Two –*OH* groups on the same carbon aldehyde is formed

$$R - CH < \stackrel{OH}{\underset{\text{Unstable}}{OH}} \stackrel{-H_2O}{\longrightarrow} R - C = O$$

Three -OH groups on the same carbon acid is formed.

$$R - C \underbrace{\bigvee_{OH}^{OH}}_{OH} \xrightarrow{-H_2O} R - C \underbrace{\bigvee_{O}^{OH}}_{acid}$$

228. (d) H_2SO_4 , Al_2O_3 and H_3PO_4 all can act as dehydrating agent.

230. (a) $H_3C - CH_2 - CH - CH_2 - OH \xrightarrow[]{\text{Conc. } H_2SO_4}{\text{dehy dration}} \rightarrow CH_3$ 2 Methyl butanol

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

$$CH_{3}$$
2-Methy I butene
Major product

233. (c)
$$CH_3CHO \leftarrow \frac{Cu}{\Delta} CH_3CH_2OH \xrightarrow{Al_2O_3} CH_2 = CH_2$$

234. (b)
$$C_6H_5 - \overset{\parallel}{C} - CH_3 \xrightarrow{\text{LiAlH}_4} C_6H_5 - \overset{\parallel}{C} H - CH_3$$

235. (d)
$$C_2H_5OH \xrightarrow{Conc} H_2SO_4 \rightarrow C_2H_4 + H_2O$$

Because conc. H_3PO_4 acts as a dehydrating agent.

238. (c)
$$C_2H_5OH \xrightarrow{NaOH} CHI_3$$
 yellow ppt.
 $CH_3OH \xrightarrow{NaOH} I_2$ No reaction

- **239.** (d) It is not acetaldehyde or acetone as does not react with hydrazine. It is not CH_3OH as does not react with Na.
- **240.** (a) The ether molecule gets protonated by the hydrogen of the acid to form protonated ether or oxonium salt.



$$+HBr \longrightarrow +Br^{-}$$

The protonated ether undergoes nucleophilic attack by halide ion (X^-) and forms alkyl alcohol and alkyl halide



This is an example of coupling reaction

243. (b) Reimer-Tiemann reaction involves the carbon carbon bond formation.



salicylaldehyde

244. (a) This is Reimer-Tiemann reaction where the electrophile is dichlorocarbene $(: CCl_2)$ generated from chloroform by the action of a base.

$$OH^- + CHCl_3 \rightleftharpoons HOH + : CCl_2^- \rightarrow Cl^- + : CCl_2$$

245. (a) Phenols are much more acidic than alcohols but less so than carboxylic acids or even carbonic acid. This is indicated by the values of ionisation constants. The relative acidity follows the order:

$$K_{a} \quad \frac{10^{-5}}{RCOOH} > \frac{10^{-7}}{H_{2}CO_{3}} > \frac{10^{-10}}{C_{6}H_{5}OH} > \frac{10^{-14}}{HOH} > \frac{10^{-18}}{ROH}$$

Uses of alcohol, Phenol and Ethers

- 1. (a) $_{\text{Glycerol}} \xrightarrow{HNO_3} \text{Glyceryltrinitrate} -$ Absorbed on →Dvnamite Kieselguhr Glyceryldinitrate
- $Acetobactoracetii \rightarrow CH_3 COOH$ (d) C_2H_5OH – 3. OCOCH 2

COOH

4

6.

Aspirin or Acetyl salicylic acid. $COOH) + n \begin{pmatrix} CH_2 - OH \\ | \\ CH_2 - OH \end{pmatrix}$ (a) n (HOOC

9. (a) Ethylene glycol is added to lowering down the freezing point of water so that it does not freeze.

(b) Power alcohol 80% petrol and 20% ethyl 10. alcohol

- (d) Glucose $\xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$ 12.
- 16. (d) Glycerol is not used as an antiseptic agent.
- (c) Denaturing can also be done by adding 0.5% 18. pyridine, petroleum naptha, CuSO₄ etc.
- (b) A mixture of glyceryl trinitrate and glyceryl 20. when absorbed on kieselgurh is dinitrate called dynamite.
- (c) Tonics have generally contains ethyl alcohol. 22.
- (c) Due to presence of methyl alcohol in liquor. 23.
- (d) An anaesthetic. 24.
- (c) Groundnut oil. 25.
- (a) $C_3H_7COOC_2H_5 \xrightarrow{Na/C_2H_5OH} C_3H_7CH_2OH$ 27. Ethy l buty rate Buty lalcohol
- 28. (a) Glycol is used as an antifreeze for automobile radiators because it lowers down the melting point of water.

Critical Thinking Questions



will undergoes a Friedel

alkylation on ortho or para position because of more electron density.

2. (c)
$$CH_2 = CH_2 + RMgI \rightarrow CH_2 - CH_2 - R \xrightarrow{HOH} OMgI$$

 $MgI(OH) + R - CH_2 - CH_2 - OH$

- (c) The liquids which decompose at its boiling 3. point can be purified by vacuum distillation. Glycerol which decomposes at its boiling point (-563K)can be distilled without decomposition at 453K under 12mm Hq pressure.
- (a) Liebermann's reaction. 4.
- 5٠ (a) 1° alcohol > 2° alcohol > 3° alcohol Boiling point of alcohols decreases as the number of branches increases.

$$6. \quad (c) \bigcirc +HI - \bigcirc +CH_3I$$

(c) $3CH_2 = CH_2 + 2KMnO_4 + 4H_2O \rightarrow$ 7.

$$CH_{2} - OH$$

$$3 + 2KMnO_{2} + 2KOH$$

$$CH_{2} - OH$$
Glycol

- (c) Correct order of dehydration in alcohols 3° > 8. $2^{\circ} > 1^{\circ}$.
- (a) Oxiran is ethylene oxide, $CH_2 CH_2$ 9.

10. (c)
$$6CH_3 - CH = CH_2 + B_2H_6 \xrightarrow{H_2O_2}$$

 $CH_3 - CH_2 - CH_2OH$

(d) Distinction between primary, secondary and 11. tertiary alcohol is done by all three methods : oxidation, Victormeyer and Lucas test.

OH

12. (b)
$$\underbrace{\bigcirc}_{v_2o_5} \underbrace{\bigcirc}_{v_2o_5} \underbrace{\bigcirc}_{v_2o_5}$$

- (a) o- and p-nitrophenols are separated by steam 13. distillation because o-nitrophenol is steam volatile while *p*-isomer is not.
- (b) Benzoic acid. 14.

15. (a)
$$R - O - R' - \frac{O_2 / \text{light}}{2}$$

$$C_2H_5 - O - CH(CH_3) - O - OH$$

16. (d)
$$CH_3OH + CH_3OH \xrightarrow{H_2SO_4(Conc)} CH_3OCH_3$$

$$CH_{3}OH + C_{2}H_{5}OH \xrightarrow{H_{2}SO_{4}(Conc)} CH_{3}OC_{2}H_{5}$$
$$C_{2}H_{5}OH + C_{2}H_{5}OH \xrightarrow{H_{2}SO_{4}(Conc)} C_{2}H_{5}OC_{2}H_{5}$$

- (b) IV > III > I > II. 17.
- (a) Cyclic ethers are called epoxides. $CH_2 CH_2$ 18.

19. (b)
$$CH_3 - CH = CH - \bigcirc OH \xrightarrow{HBr} OH$$

$$CH_3 - CH_2 - CH_1$$

Br

20. (c) $\bigcirc OCH_3$ on $KMnO_4$ oxidation does not

give benzoic acid.

21. (c) Chromic anhydride in glacial acetic acid is the best reagent to convert pen-3-en-2-ol into pent-3-in-2-one.

22. (a)
$$-\overset{\mid}{C} - \overset{\mid}{C} - \overset{\mid}{H} - \overset{\mid}{H} - \overset{\mid}{C} - \overset{\mid}{C} - \overset{\mid}{H} - \overset{\mid}{$$

In all cases intermediate is carbonium ion, and there may be 1, 2-hydride or 1, 2-methyl shift to form more stable carbonium ion.

Assertion & Reason

- **3.** (a) It is correct that phenol is more reactive than benzene.
- 4. (c) It is correct that sodium phenoxide (sodium salt of phenol) and CO_2 on heating from sodium salicylate. This is known as Kolbe's reaction. Ethanol does not respond to this reaction. Therefore, assertion is true. But the reason that phenoxide ion is more basic than ethoxide ion is not correct.
- 5. (c) Lucas reagent is a mixture of anhydrous $ZnCl_2$ and coc. *HCl* is used for the distinction of monohydric alcohol. Tertiary alcohols on addition produce a precipitate immediately while secondary alcohols produce ppt. after 5 minutes. Primary alcohols do not produce any precipitate. Therefore, assertion is true but reason is false.
- 6. (a) Phenols on treatment with neutral $FeCl_3$ solution produce purple colour, resorcinol contains phenolic group hence in treatment with $FeCl_3$ solution it gives purple colour. Here both assertion and reason are correct and reason is a correct explanation of assertion.
- 7. (b) Glycerol is purified by distillation under reduced pressure because it decomposes on heating below its melting point. It is a trihydric alcohol. Here, both assertion and reason are true but reason is not a correct explanation of assertion.

Alcohol, Phenol and Ethers 1251

- (a) Alcohols and phenols can be distinguished by treating with *NaOH*. Phenols react with *NaOH* to produce sodium phenoxide because phenols are acidic and alcohols are neutral. Both assertion and reason are true and reason is correct explanation.
- **9.** (b) Zeolites are shape-selective porous solid acid catalysts, their catalytic activity originates from the presence of highly acidic Al O(H) Si hydroxyl in the framework.

$$\textbf{10.} \quad \textbf{(a)} \quad C_6H_5CH_2OCH_3 \xrightarrow{H^+} C_6H_5CH_2^+ + CH_3OH$$

 $\xrightarrow{\Gamma} C_6 H_7 C H_2 I$

This can be explained on the basis of $S_N 1$ mechanism. The carbonium ion produced being benzylium ion. Since this type is more stable than alkylium ion.

- (c) Lower the value of *pKa*, more acidic will be the compound. Acetic acid is more acidic than phenol. This indicates that carboxylate ion should be more stable than the phenoxide ion and it is clear that carboxylate ion has more equivalent resonating structures than the phenoxide ion.
- **12.** (a) The conversion of sugar into ethyl alcohol by yeast is called alcoholic fermentation.

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

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

- 13. (b) The tendency to show *H*-bonding decreases with increasing hydrophobic character of carbon chain. The hydrophobic character of carbon chain increases with he length of carbon chain.
- 14. (e) Ethyl alcohol forms azeotropic mixture with water which distils with unchanged composition (about 75% ethanol) and thus absolute alcohol cannot be obtained by simple distillation.
- 15. (e) The dehydration of *t*-butanol involves the formation of 3° carbocation which is more stable than 1° carbocation in *n*-butanol. Thus, tendency to lose water becomes more in *t*-butanol.
- 16. (c) A mixture of conc. HCl + anhyd. ZnCl₂ is called Lucas reagent.
- 17. (e) Electron withdrawing groups such as -NO2, -CN, -X, increase the acidity. Greater the number of electron withdrawing groups more is the acidic character *i.e.* 2, 4, 6trinitrophenol is more acidic than 4nitrophenol.

- 18. (b) Phenols cannot be converted into esters by direct reaction with carboxylic acids since phenols are less nucleophilic than alcohols.
- 19. (b) Alcohol which forms the more stable carbocation undergoes dehydration more readily. Since tert-butyl alcohol forms more stable tert-butyl cation, therefore, it undergoes dehydration most readily than propanol.
- 20. (e) The ease of dehydration of alcohols can be explained on the basis of stability of the intermediate carbocation. Greater the stability of the carbonation formed, greater will be the rate of reaction. The order of stability of carbocation formed is

$$CH_{3} - CH_{3} \rightarrow CH_{3} \rightarrow CH_{3} \rightarrow H_{3}C - C_{1} \rightarrow CH_{3} - C_{1} \rightarrow CH_{3} - C_{1} \rightarrow CH_{3} - C_{1} \rightarrow H_{1} \rightarrow CH_{3} - C_{1} \rightarrow H_{1} \rightarrow CH_{3} - C_{1} \rightarrow H_{1} \rightarrow CH_{1} \rightarrow C$$

This is due to the electron releasing (+I) effect of the alkyl group. Therefore the ease of dehydration of alcohols follows the order.

Tertiary > secondary > primary alcohol.

- **21.** (c) Benzoylation in phenols is usually carried out in the presence of aqueous *NaOH* because benzoyl chloride is not readily hydrolysed by alkalies.
- **22.** (b) In phenols, the lone pairs of electrons on the oxygen atom are delocalised over the benzene ring due to resonance and hence are not easily available for protonation. On the other hand, in alcohols, the lone pairs of electrons on oxygen atom are localized due to the absence of resonance and hence are easily available for ptotonation.

- 25. (c) Nucleophilic attack of phenolate ion through the ortho-carbon atom occurs on CCl₄ to form an intermediate which on hydrolysis gives salicylic acid.
- **26.** (a) Victor-Meyer's test is used to distinguish primary, secondary and tertiary alcohols.



- **28.** (b) Removal of two molecules of water gives a product which tautomerises to yield acroleinan α , β -unsaturated aldehyde.
- 29. (b) Depending upon whether the alkyl halide and the alkoxide ion carry the same or different alkyl groups both symmetrical and unsymmetrical ethers can be prepared by Williamsons synthesis.
- **30.** (c) Ethers being Lewis bases form etherates with Lewis acids.
- **31.** (d) $(CH_3)_3 CONa$ and CH_3CH_2Br react to form $(CH_3)_3C O CH_2CH_3$. Good yields of ethers are obtained when primary alkyl halides are treated with alkoxides derived from any alcohol. 1°, 2° or 3°.

- **23.** (c) *p*-Nitrophenolate ion is more stable than phenolate ion.
- 24. (b) Nitrous acid gives nitrosomine ion (NO⁺) which attacks phenol at less hindered *p*-position of form *p*-nitrosophenol which is a tautomer of *p*-benzoquinone monoxide.

 $N = O \equiv$ -NOH HO p*p*-Benzoquinone

1.
$$CH_3 - CH - CH_3 \xrightarrow{PB_{0}} A \xrightarrow{M_{g}} B \xrightarrow{CH_2 - CH_2} C$$

 OH
 $\xrightarrow{H_{2O}} D$ Here, D is [BVP 2004]
(a) $CH_3 - CH - O - CH_2 - CH_3$
 CH_3
(b) $CH_3 - O - CH - CH_2CH_3$
 CH_3
(c) $CH_3 - CH - CH_2CH_2OH$
 CH_3
(d) $CH_3 - CH_2 - CH_2OH$
 CH_3
2. Phenol is more acidic than [Pb. CET 2003]
 $(c) C_2H_2$ (d) Both (a) and (c)
9.
(c) C_2H_2 (d) Both (a) and (c)
9.
(c) C_2H_2 (d) Both (a) and (c)
9.
3. In the reaction,
 $C_{\theta}H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3COON_{\theta}} (A)$ product (A)
is [Pb. CET 2000]
(a) Acetaldehyde (b) Cinnamic acid
(c) β -nephthol (d) Phenol
4. The correct order of ease of dehydration of following is
 $\overrightarrow{OH} - OH \xrightarrow{II} OH \xrightarrow{II} OH$
(a) $I > II > III$ (b) III > II > I
(c) $I > III > III$ (b) III > I > I
(c) $I > III > III$ (c) $I = III > II$
(c) $I > III > II$ (d) $III > I > I$
5. PCI_5 reacts with a compound containing[Pb. CET 2002]10.
(a) $-SO_3$ group (b) $- OH$ group
(c) $-NO_3$ group (d) $-NO$ group
6. Cumene process is the most important commercial method for the manufacture of reaction of polymeric o

- commercial method for the manufacture of
phenol. Cumene is**[KCET 2004]**(a) 1-methyl ethyl benzene(b)Ethyl benzene(c) Vinyl benzene(d) Propyl benzene
- 7. The compound X in the reaction [Roorkee 1999]



Self Evaluation Test -26



The order of solubility of alkanols in water is

(b)

- (a) Propanol < Butanol > Pentanol
- (b) Propanol > Butanol > Pentanol
- (c) Propanol > Butanol < Pentanol
- (d) Propanol = Butanol = Pentanol

11. In the following compounds

(a)



The order of acidity is [IIT-JEE 1996] (a) III > IV > I > II(b) I > IV > III > II(c) II > I > III > IV(d) IV > III > I > IIButanal with dilute *NaOH* gives [UPSEAT 2000] 12. OH(a) $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2$ (b) $CH_3CH_2CH_2 \overset{\parallel}{C}CH_2 CH_2CH_2CHO$ (c) $OHCCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2$ OH(d) $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CHCHO$ H CH₂ CH 2 The correct order of the solubility of the different 13.

alcohols in water is [Pune CET 1998] (a) *n*-propyl alcohol > ethyl alcohol > *n*-butyl alcohol

(b) Ethyl alcohol > n-butyl alcohol > n-propyl alcohol

(c) n-butyl alcohol > n-propyl alcohol > ethyl alcohol

(d) Ethanol > *n*-propanol > *n*-butyl alcohol

 Which one of the following will most readily be dehydrated in acidic condition[IIT-JEE (Screening) 2000]



(c)

 Which of the following compounds will be most easily attacked by an electrophile[CBSE PMT 1998, 99]

(d)



- **16.** Fittig's reaction produces
 - (a) Alkane (b) Alcohol
 - (c) Diphenyl (d) Diethyl ether
- **17.** 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









1. (c) The reaction sequence is as follows $CH_3 - CH - CH_3 \xrightarrow{PBr_3} CH_3 - CH - CH_3 \xrightarrow{M_g} CH_3 - CH_3 \xrightarrow{M_g} CH_3 \xrightarrow{M_g}$

$$(CH_{3})_{2}CH.CH_{2}CH_{2}OMgBr \xrightarrow{H_{2}O}_{-Mg(OH)Br} (CH_{3})_{2}CH.CH_{2}CH_{2}OMgBr \xrightarrow{H_{2}O}_{-Mg(OH)Br} (CH_{3})_{2}CH.CH_{2}CH_{2}OH \xrightarrow{[D]}_{\text{isopenty lalcohol}} (CH_{3})_{2}CH.CH_{2}CH_{2}OH$$

- 2. (d) Methoxy group due to +*I* effect increase electron density on *OH* group, thus making it less acidic. Thus *o*-methoxy phenol and acetylene are less acidic than phenol, *p*-nitrophenol is more acidic than phenol
- 3. (b) Perkin reaction is the condensation reaction in which an aromatic aldehyde is heated with an aromatic aldehyde is heated with an anhydride of an aliphatic acid in presence of sodium salt of same acid to form α , β unsaturated acid.

$$\begin{array}{c} C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa} \\ \text{Benzaldehy de} & \text{acetic anhy dride} \end{array}$$

$$C_6H_5CH = CHCOOH + CH_3COOH \\ \text{cinnamic acid} & \text{acetic acid} \end{array}$$

4. (b) The correct order of stability of carbocation is as follows



5. (b) PCl_5 is used in organic chemistry to replace the -OH group by -Cl and carbonylic oxygen by $(-Cl_2)$.





It is Kolbe's reaction.





- (b) Propanol > Butanol> Pentanol
 The solubility of alcohols in water decreases as the molecular mass increases. As the size of alkyl group increases, hydrophobic character increases, Hence solubility decreases.
- 11. (d) IV > III > I > II. $-NO_2$ group is electron withdrawing group while $-CH_3$ group is electron releasing group.

12. (d)
$$2CH_3 - CH_2 - CH_2 - CHO + \text{dil. } NaOH \rightarrow$$

 $OH CHO$
 $CH_3CH_2CH_2 - CH - CH_2 - CH_3$
 H

- 13. (d) Ethanol > n-propanol > n-butyl alcoholSolubility of alcohols in water decreases as the size of alkyl group increases because tendency to form hydrogen bonding decreases.
- 14. (a) Aldols (β -hydroxy aldehydes or β -hydroxy ketones) readily undergo dehydration to form α , β -unsaturated aldehydes or ketones.



- 15. (c) Phenol is most easily attacked by an electrophile because presence of -OH group increases electron density at o- and p-positions.
- **16.** (c) $2C_6H_5Cl + 2Na \xrightarrow{\text{Dry}} C_6H_5 C_6H_5 + 2NaCl$ diphenyl

