4

ORGANIC CHEMISTRY

ALCOHOLS, PHENOLS AND ETHERS

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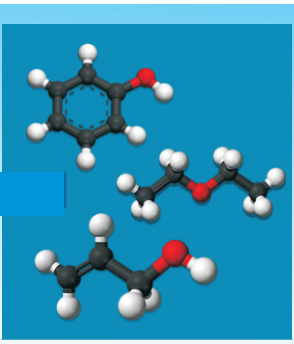


ALCOHOLS

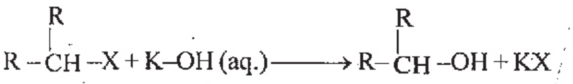
Methods of preparation

1. From alkyl halides (Hydrolysis) : Alkyl halides on hydrolysis with aq. KOH/moist Ag_2O or AgOH form alcohols.

The hydrolysis occurs by nucleophilic substitution reaction.

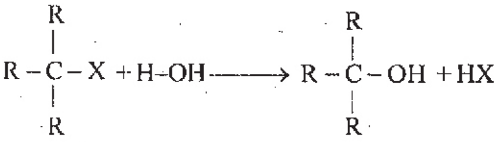
$$R{-}CH_2{-}X + AgOH(aq.) \longrightarrow R{-}CH_2{-}OH + AgX$$

1° Alcohol



$$R-\overset{R}{\overset{|}{C}H}-X + K{-}OH\,(aq.) \longrightarrow R-\overset{R}{\overset{|}{C}H}-OH + KX$$

Alkyl halide 2° Alcohol

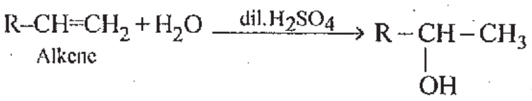


$$R-\underset{R}{\underset{|}{\overset{R}{\overset{|}{C}}}}-X + H{-}OH \longrightarrow R-\underset{R}{\underset{|}{\overset{R}{\overset{|}{C}}}}-OH + HX$$

3° Alcohol

2. From alkenes :

(i) Hydration of alkenes



$$R{-}CH{=}CH_2 + H_2O \xrightarrow{dil.H_2SO_4} R-\underset{OH}{\underset{|}{CH}}-CH_3$$

Alkene 2° Alcohol

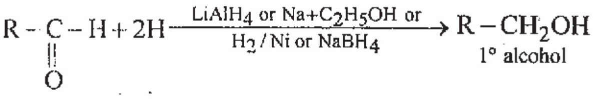
(ii) Hydroboration-oxidation

The addition takes place in accordance with the Markovnikov's rule.

$$3CH_3-CH=CH_2+B_2H_6 \xrightarrow{THF} 3CH_3CH_2CH_2OH+H_3BO_3$$

The addition takes place in accordance with **anti-Markovnikov's rule.**

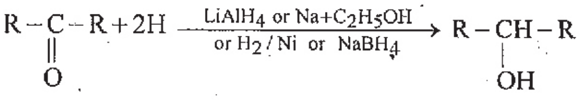
3. By reduction of carbonyl compounds :



$$R-\underset{O}{\underset{\|}{C}}-H+2H \xrightarrow[H_2/Ni \text{ or } NaBH_4]{LiAlH_4 \text{ or } Na+C_2H_5OH \text{ or}} R-CH_2OH$$

1° alcohol

Aldehyde



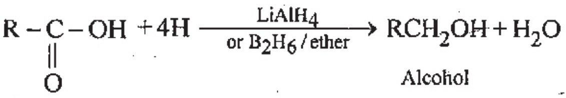
$$R-\underset{O}{\underset{\|}{C}}-R+2H \xrightarrow[\text{or } H_2/Ni \text{ or } NaBH_4]{LiAlH_4 \text{ or } Na+C_2H_5OH} R-\underset{OH}{\underset{|}{CH}}-R$$

Ketone 2° alcohol

Note:

3° alcohol cannot be obtained by this method

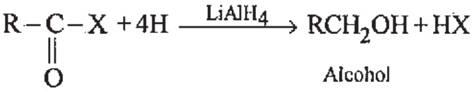
4. By reduction of acids and their derivatives :



$$R-\underset{O}{\underset{\|}{C}}-OH+4H \xrightarrow[\text{or } B_2H_6/\text{ether}]{LiAlH_4} RCH_2OH+H_2O$$

Alcohol

Carboxylic acid



$$R-\underset{O}{\underset{\|}{C}}-X+4H \xrightarrow{LiAlH_4} RCH_2OH+HX$$

Alcohol

Acid halide

$$R-\underset{O}{\underset{\|}{C}}-OR'+4H \xrightarrow{LiAlH_4} RCH_2OH+R'OH$$

Alcohol

Ester

$$(RCO)_2O+8H \xrightarrow{LiAlH_4} 2RCH_2OH+H_2O$$

Acid anhydride Alcohol

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

5. From Grignard reagent

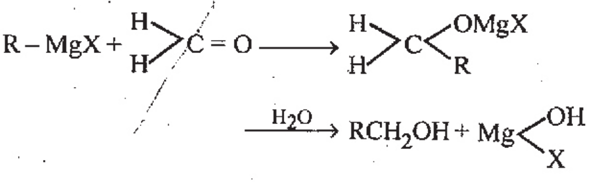
(i) Primary alcohol :

(a) With oxygen :

$$2R-Mg-X+O_2 \xrightarrow{\Delta} 2R-O-Mg-X \xrightarrow{2HOH} 2ROH + 2Mg(X)OH$$

Primary alcohol

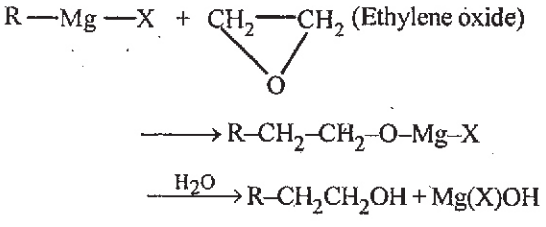
(b) With formaldehyde :



$$R-MgX+\frac{H}{H}{>}C=O \longrightarrow \frac{H}{H}{>}C{<}\frac{OMgX}{R} \xrightarrow{H_2O} RCH_2OH+Mg{<}\frac{OH}{X}$$

Alcohol

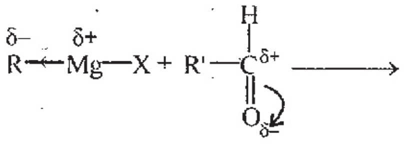
(c) With ethylene oxide :



$$R-Mg-X + \underbrace{CH_2-CH_2}_{O} \text{ (Ethylene oxide)} \longrightarrow R{-}CH_2{-}CH_2{-}O{-}Mg{-}X \xrightarrow{H_2O} R{-}CH_2CH_2OH+Mg(X)OH$$

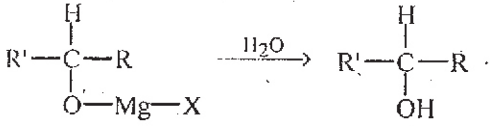
Alcohol

(ii) Secondary and tertiary alcohols :



$\overset{\delta-}{R}\leftarrow\overset{\delta+}{Mg}-X + R'-\underset{O}{\underset{\|}{\overset{H}{\overset{|}{C^{\delta+}}}}} \longrightarrow$

Aldehyde



$R'-\underset{O-Mg-X}{\underset{|}{\overset{H}{\overset{|}{C}}}}-R \xrightarrow{H_2O} R'-\underset{OH}{\underset{|}{\overset{H}{\overset{|}{C}}}}-R$

(Secondary alcohol)

- If carbonyl compound is ketone, product will be tertiary alcohol.

6. From primary amines :

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

7. Hydrolysis of ether :

$\underset{\text{Ether}}{ROR'} + HOH \xrightarrow{dil.H_2SO_4} \underset{\text{alcohol}}{ROH + R'OH}$

Physical Properties

(i) Melting point and Boiling point ∝ molecular mass

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

(ii) Boiling point of alcohols are higher than corresponding ethers due to H–bonding.

Chemical Properties

A. Reactions involving the cleavage of the O-H bond

The general order of reactivity of alcohols in this type of reaction is :–

Primary > Secondary > Tertiary

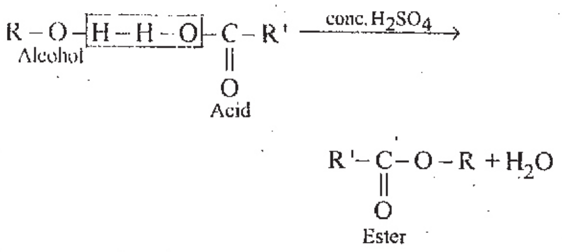
1. Reaction with metals : On reaction with active metals like – Na, K, Ca, Mg, Al, etc., they liberate hydrogen gas.

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

The acidic order of alcohols is

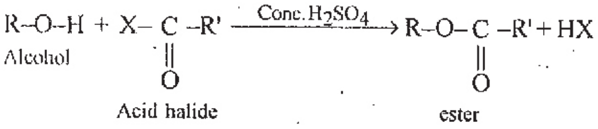
MeOH > 1° > 2° > 3°

2. Reaction with carboxylic acids (Esterification) :

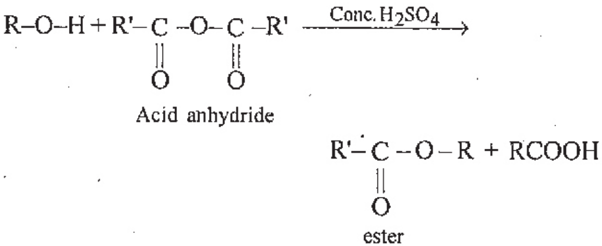


$\underset{\text{Alcohol}}{R-O-}\boxed{H-H-O}-\underset{\underset{\text{Acid}}{O}}{\underset{\|}{C}}-R' \xrightarrow{conc.H_2SO_4} R'-\underset{\underset{\text{Ester}}{O}}{\underset{\|}{C}}-O-R + H_2O$

3. Reaction with acid derivatives (Acetylation) :



$\underset{\text{Alcohol}}{R-O-H} + X-\underset{\underset{\text{Acid halide}}{O}}{\underset{\|}{C}}-R' \xrightarrow{Conc.H_2SO_4} R-O-\underset{\underset{\text{ester}}{O}}{\underset{\|}{C}}-R' + HX$



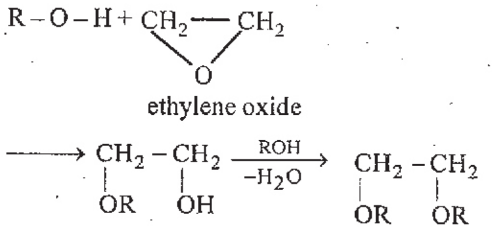
$R-O-H + R'-\underset{O}{\underset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}-R' \xrightarrow{Conc.H_2SO_4}$

Acid anhydride

$R'-\underset{O}{\underset{\|}{C}}-O-R + RCOOH$

ester

4. Reaction with ethylene oxide :



$R-O-H + CH_2-CH_2$ (ethylene oxide, O bridging) $\longrightarrow \underset{OR}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH_2}} \xrightarrow[-H_2O]{ROH} \underset{OR}{\underset{|}{CH_2}}-\underset{OR}{\underset{|}{CH_2}}$

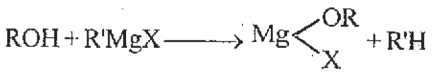
ethylene oxide

1, 2-dialkoxy ethane

5. Reaction with diazomethane :

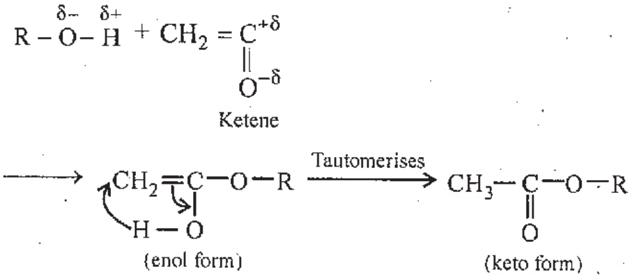
$R-O-H + \underset{\text{Diazomethane}}{CH_2N_2} \longrightarrow \underset{\text{(ether)}}{R-O-CH_3}$

6. Reaction with Grignard reagent :



$ROH + R'MgX \longrightarrow Mg\langle^{OR}_{X} + \underset{\text{Alkane}}{R'H}$

7. Reaction with ketene :



$R-\overset{\delta-}{O}-\overset{\delta+}{H} + CH_2=\underset{O^{-\delta}}{\underset{\|}{C^{+\delta}}}$

Ketene

$\longrightarrow \underset{\text{(enol form)}}{CH_2=\underset{H-O}{\underset{|}{C}}-O-R} \xrightarrow{\text{Tautomerises}} \underset{\text{(keto form)}}{CH_3-\underset{O}{\underset{\|}{C}}-O-R}$

B. Reaction involving the cleavage of C-OH bond :

The order of reactivity in this type of reaction is –
3° alcohol > 2° alcohol > 1° alcohol

1. Reaction with dry HX (Groove's process)

Reactivity order of halogen acid is HI > HBr > HCl

$R-OH + HX \xrightarrow{Anhydrous\ ZnCl_2} \underset{\text{Alkyl halide}}{R-X} + H_2O$

2. Reaction with PCl_5 :

$R-OH + PCl_5 \longrightarrow \underset{\text{Chloro alkane}}{R-Cl} + POCl_3 + HCl$

3. Reaction with PCl_3 :

$3R-OH + PCl_3 \longrightarrow \underset{\text{Chloro alkane}}{3R-Cl} + H_3PO_3$

4. Reaction with $SOCl_2$ (Darzen reaction) :

$R-OH + \underset{\text{Thionyl chloride}}{SOCl_2} \xrightarrow{Pyridine} \underset{\text{Chloroalkane}}{R-Cl} + SO_2\uparrow + HCl\uparrow$

5. Reaction with ammonia :

$R-OH + NH_3 \xrightarrow[\substack{300°C \\ \text{or} \\ Al_2O_3}]{anhy.ZnCl_2} \underset{\text{Alkylamine}}{RNH_2} + H_2O$

6. Reaction with H_2SO_4 :

(i) $C_2H_5OH + H_2SO_4 \xrightarrow{110^{\circ}C} \underset{\text{Ethyl hydrogen sulphate}}{CH_3CH_2OSO_3H}$

(ii) $2CH_3CH_2OSO_3H \xrightarrow{\Delta} \underset{\text{(Diethyl sulphate)}}{(C_2H_5)_2SO_4} + H_2SO_4$

(iii) $\underset{\text{(excess)}}{CH_3-CH_2-OH} + \underset{\text{(conc.)}}{H_2SO_4} \xrightarrow{140^{\circ}C} \underset{\text{Diethyl ether}}{CH_3-CH_2-\ddot{\underset{..}{O}}-CH_2-CH_3}$

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

C. General Reaction of Alcohols

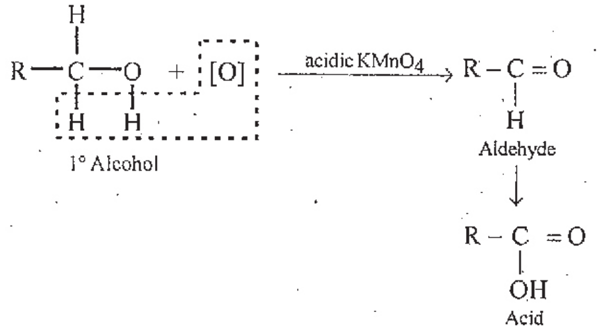
1. Oxidation :

(i) Primary alcohol initially forms aldehyde on oxidation and on further oxidation forms respective acid.

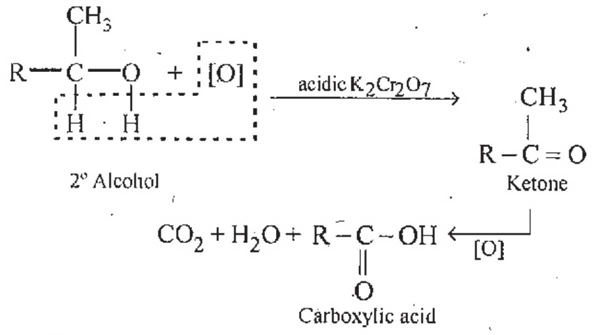
(ii) Secondary alcohol initially forms respective ketone on oxidation which on further oxidation forms acid with less no. of carbon atoms. Oxidation of ketone is slightly difficult than aldehyde due to stability so, we use strong oxidising agent for oxidation.

(iii) Tertiary alcohols are resistant to oxidation in normal conditions but on taking strongest oxidising agent like chromic acid in dilute nitric acid they form less carbon ketone.

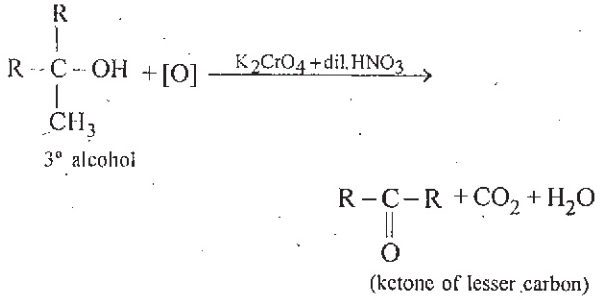
(iv) For oxidation of 1° alcohol, acidic $KMnO_4$ is used as oxidant while for 2° alcohol acidic $K_2Cr_2O_7$ is used.



$R-\overset{H}{\underset{H}{C}}-\underset{H}{O} + [O] \xrightarrow{\text{acidic } KMnO_4} R-\underset{H}{C}=O \rightarrow R-\underset{OH}{C}=O$



$R-\overset{CH_3}{\underset{H}{C}}-\underset{H}{O} + [O] \xrightarrow{\text{acidic } K_2Cr_2O_7} R-\overset{CH_3}{C}=O \xrightarrow{[O]} CO_2 + H_2O + R-\underset{O}{\underset{\|}{C}}-OH$



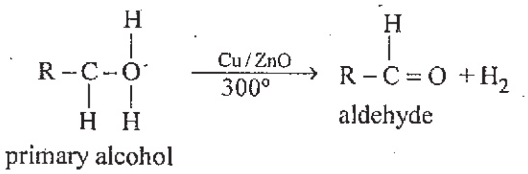
$R-\overset{R}{\underset{CH_3}{C}}-OH + [O] \xrightarrow{K_2CrO_4 + \text{dil. } HNO_3} R-\underset{O}{\underset{\|}{C}}-R + CO_2 + H_2O$

To stop the reaction at aldehyde or ketone stage, milder oxidising agents like CrO_3 or PCC (pyridinium chloro chromate) are used. (PCC is better option)

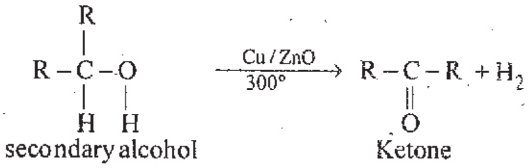
2. Reduction :

$R-O-H + 2HI \xrightarrow[150^{\circ}C]{\text{Red P}} R-H + H_2O + I_2$

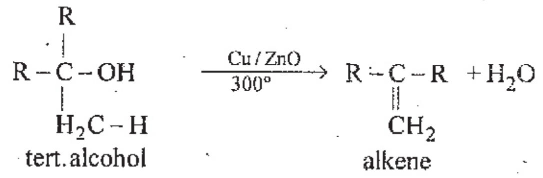
3. Dehydrogenation :



$R-\underset{H}{C}H-\underset{H}{O} \xrightarrow[300^{\circ}]{Cu/ZnO} R-\overset{H}{C}=O + H_2$



$R-\overset{R}{\underset{H}{C}}-\underset{H}{O} \xrightarrow[300^{\circ}]{Cu/ZnO} R-\underset{O}{\underset{\|}{C}}-R + H_2$

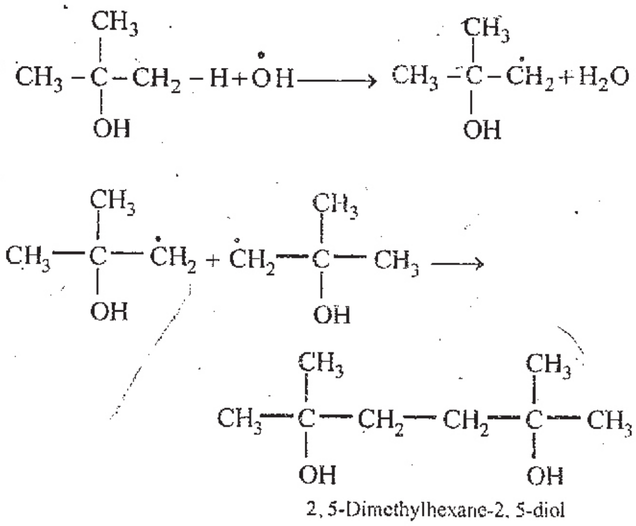


$R-\overset{R}{\underset{H_2C-H}{C}}-OH \xrightarrow[300^{\circ}]{Cu/ZnO} R-\underset{CH_2}{\underset{\|}{C}}-R + H_2O$

4. Oxidation through Fenton's reagent :

Higher and branched alcohols are converted into diols through Fenton's reagent. $(FeSO_4 + H_2O_2)$ is Fenton's reagent.

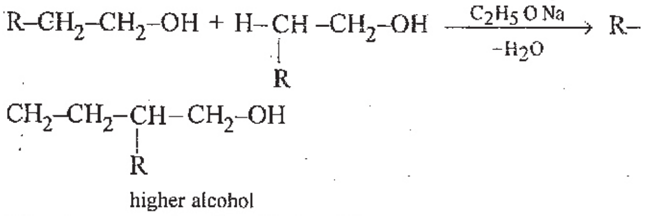
$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + \bar{O}H + \dot{O}H$



$CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_2-H + \dot{O}H \longrightarrow CH_3-\overset{CH_3}{\underset{OH}{C}}-\dot{C}H_2 + H_2O$

$CH_3-\overset{CH_3}{\underset{OH}{C}}-\dot{C}H_2 + \dot{C}H_2-\overset{CH_3}{\underset{OH}{C}}-CH_3 \longrightarrow CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_2-CH_2-\overset{CH_3}{\underset{OH}{C}}-CH_3$

5. Self condensation :



$R-CH_2-CH_2-OH + H-\underset{R}{CH}-CH_2-OH \xrightarrow[-H_2O]{C_2H_5\overset{\ominus}{O}\overset{\oplus}{Na}} R-CH_2-CH_2-\underset{R}{CH}-CH_2-OH$

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

6. Dehydration : Primary alcohols when heated in presence of an acid catalyst (usually H_2SO_4) undergo intermolecular dehydration to form ethers.

$$R{-}OH + HO{-}R \xrightarrow{H^+,\ heat} R{-}O{-}R$$

Distinction between Primary, Secondary and Tertiary Alcohols

1. By Oxidation reaction : Primary alcohols give aldehyde on oxidation, secondary alcohols give ketone and tertiary alcohols are resistant to oxidation.

2. By Catalytical Oxidation / Dehydrogenation :: Primary alcohols give aldehydes on oxidation, secondary alcohols give ketones and tertiary give alkenes when treated with Cu.

3. Lucas test : A mixture of (anhydrous $ZnCl_2$ + Conc. HCl) is called as **Lucas Reagent**.

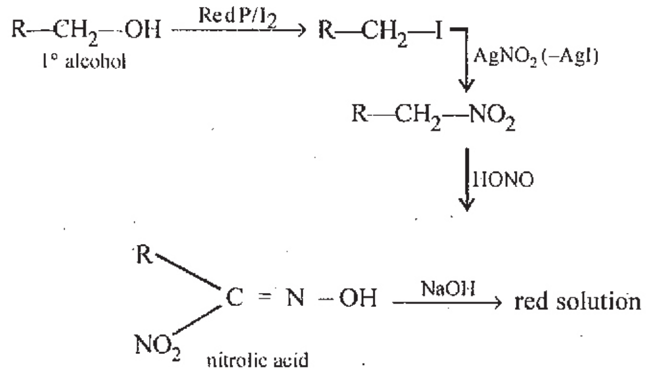
(i) 3° alcohols give white ppt. with Lucas reagent in 2–3 seconds only.

(ii) 2° alcohols take 9–10 minutes.

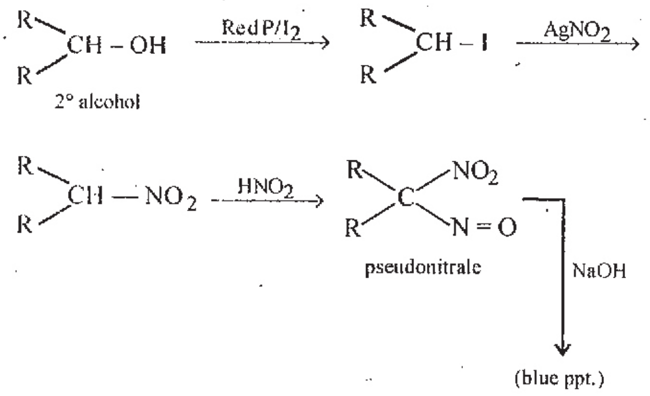
(iii) 1° alcohols does not give white ppt. at room temperature.

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

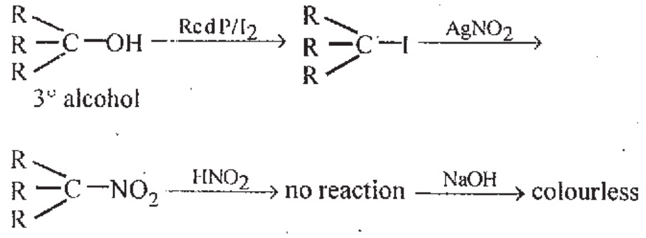
(a)



(b)



(c)



• Difference between Methanol and Ethanol

Methanol	Ethanol
1. When CH_3OH is heated on Cu, it gives formalin like smell	1. Ethanol does not give formalin like smell.
2. When CH_3OH is heated with salicylic acid in H_2SO_4 (conc.) then methyl salicylate is formed which has odour like winter green oil	2. No such odour is given by ethanol
3. It does not give haloform or Iodoform test.	3. It gives haloform test.

• Interconversions

(1) Conversion of lower primary alcohol into higher primary alcohol.

(a) By cyanide synthesis :

$$RCH_2OH \xrightarrow{P+I_2} RCH_2I \xrightarrow{KCN} RCH_2CN$$

$$\xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni\ or} RCH_2CH_2NH_2 \xrightarrow{HNO_2} RCH_2CH_2OH$$

(b) By Grignard synthesis :

$$RCH_2OH \xrightarrow{P+I_2} RCH_2I \xrightarrow[Ether]{Mg} RCH_2MgI$$

$$\xrightarrow{HCHO} RCH_2CH_2OMgI \xrightarrow{H_2O} RCH_2CH_2OH$$

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

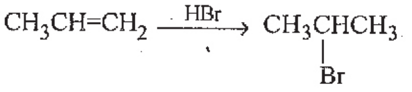
$$RCH_2OH \xrightarrow{[O]} RCHO \xrightarrow{[O]} RCOOH \xrightarrow{NaOH}$$

$$RCOONa \xrightarrow{Soda-lime} RH \xrightarrow[UV]{Cl_2} RCl$$

$$\xrightarrow{KOH(Aq.)} ROH$$

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

$$\underset{n\text{–propyl alcohol}}{CH_3CH_2CH_2OH} \xrightarrow{SOCl_2} CH_3CH_2CH_2Cl \xrightarrow{alc.KOH}$$



$$CH_3CH{=}CH_2 \xrightarrow{HBr} CH_3\underset{\underset{Br}{|}}{C}HCH_3$$

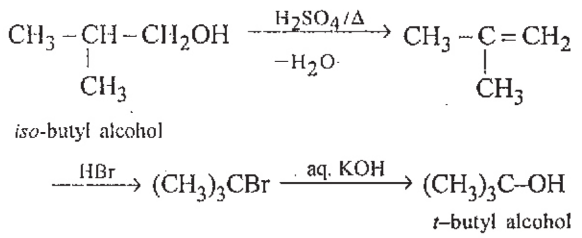
$$\xrightarrow{aq.\ KOH} \underset{isopropyl\ alcohol}{(CH_3)_2CHOH}$$

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

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

$$\underset{(intermediate)}{CH_3{-}CH_2OMgBr} \xrightarrow{H_3O^+} \underset{t\text{–butyl alcohol}}{(CH_3)_3C{-}OH}$$

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



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH \xrightarrow[-H_2O]{H_2SO_4/\Delta} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 \xrightarrow{HBr} (CH_3)_3CBr \xrightarrow{aq.\ KOH} (CH_3)_3C{-}OH$$

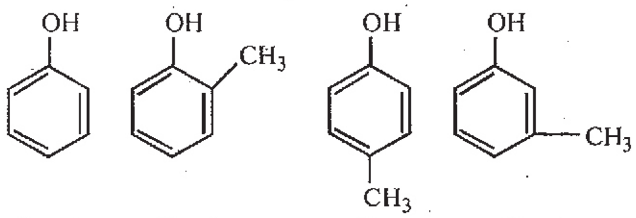
iso-butyl alcohol

t–butyl alcohol

PHENOLS

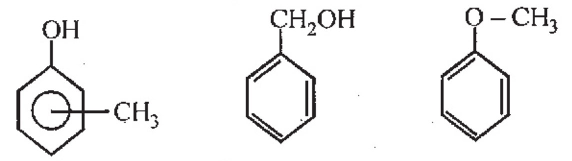
Introduction

Compounds in which hydroxyl group is directly attached to the carbon atom of the aromatic ring.



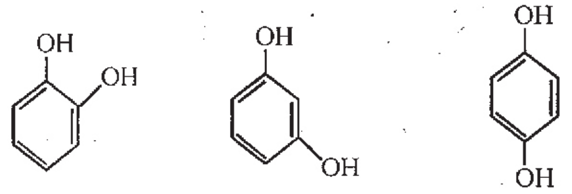
Phenol *o*-Cresol *p*-Cresol *m*-Cresol

Like other classes of organic compounds, phenols also show isomerism. The three cresols (*o*–, *m*–, and *p*–) are position isomers while benzyl alcohol and anisole (C_7H_8O) are functional isomers.



o-, *m*- and *p*-Cresols Benzyl alcohol Anisole

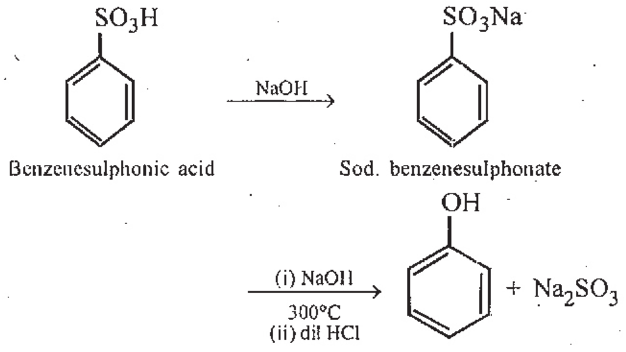
Similarly, dihydroxybenzene (dihydric phenols) may exist in three isomeric forms.



Catechol (1,2-Dihydroxy benzene) Resorcinol (1,3-Dihydroxy benzene) Quinol (1,4-Dihydroxy benzene)

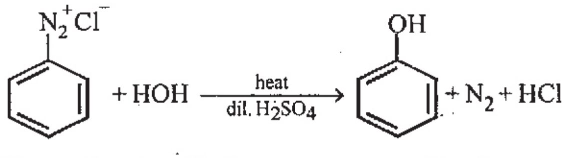
Methods of preparation

(i) With NaOH : By fusing the sodium salt of benzenesulphonic acid with NaOH.



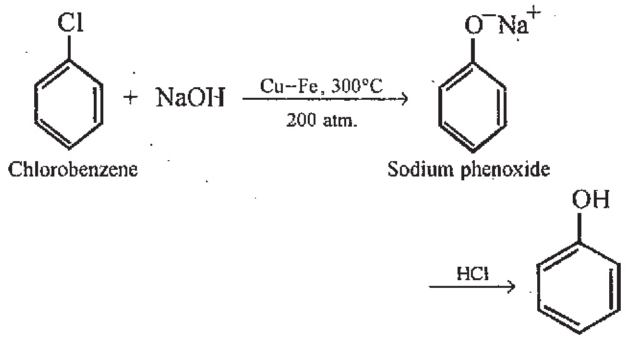
Benzenesulphonic acid Sod. benzenesulphonate Phenol

(ii) With Benzene diazonium chloride : By adding benzene diazonium chloride to a large volume of boiling dilute H_2SO_4.



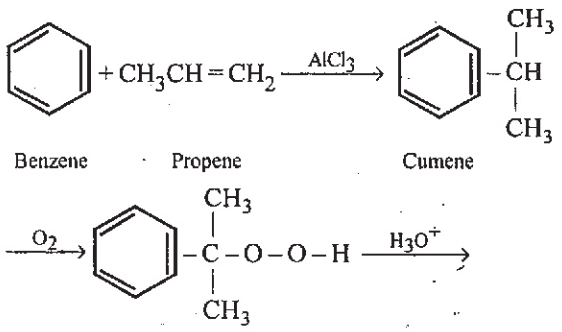
Benzenediazonium chloride Phenol

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



Chlorobenzene Sodium phenoxide Phenol

(iv) From cumene hydroperoxide



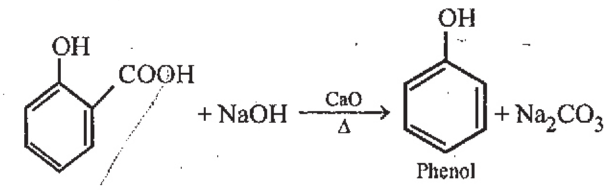
Benzene Propene Cumene

Cumene hydroperoxide

$C_6H_5OH + (CH_3)_2CO$

Phenol Acetone

(v) By distilling a phenolic acid with soda lime (Decarboxylation) :



Salicylic acid Phenol

(vi) By Rasching process :

$$C_6H_6 + HCl + \frac{1}{2}O_2 \xrightarrow[200^\circ C]{Cu-Fe} C_6H_5Cl + H_2O$$

$$C_6H_5Cl + \underset{(steam)}{HOH} \xrightarrow[450^\circ C]{SiO_2} C_6H_5OH + HCl$$

Physical Properties :

(i) Colourless crystalline solid with carbolic smell.
(ii) m.p. = 40°C b.p. = 182°C
(iii) Turns reddish brown when exposed in air.
(iv) Soluble in organic solvent, partially soluble in cold water.

Chemical Properties

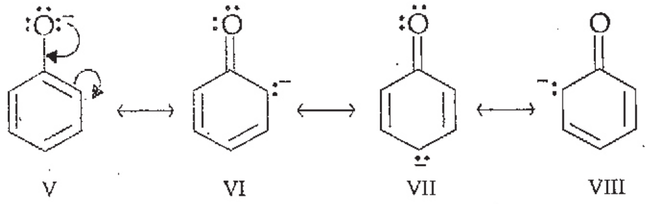
1. Acidic Character

The most characteristic property of phenols is their acidity. Phenols are more acidic than alcohols which are even more weakly acidic than water, but phenols are less acidic than carboxylic acids.

R—COOH > Ar—OH > H—OH > R—OH **(Acidic character)**

(*i*) Greater acidity of a phenol than an alcohol is due to possibility of resonance in phenol which leads to electron-deficient oxygen atom.

(*ii*) Once hydrogen atom is removed from phenol, the ion (phenoxide) is very much stabilized due to delocalization of its negative charge.



Resonance in phenoxide ion
(note that structures VI to VIII are equivalent)

Remember that phenoxide ion is very much more stable than the parent compound phenol because phenoxide ion does not involve charge separation, while in phenol three equivalent resonanting structures (II to IV) involve charge separation.

(*iii*) Electron-withdrawing substituents increase the acidity of phenols ; while electron-releasing substituents decrease acidity. Thus substituents affect acidity of phenols in the same way as they affect acidity of carboxylic acids ; it is of course, opposite to the way these groups affect basicity of amines.

2. Reactions of - OH group

(i) Action of ferric chloride : Unlike alcohols, phenols give characteristic colour with neutral ferric chloride solution.

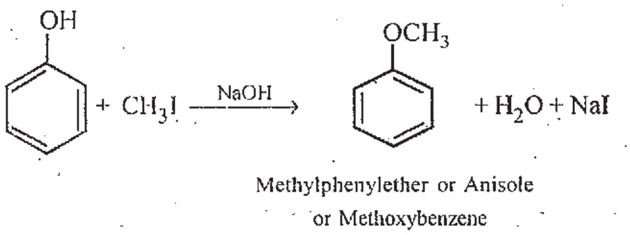
(ii) Reduction with zinc dust :

$$C_6H_5OH + Zn \xrightarrow{\text{distil}} C_6H_6 + ZnO$$

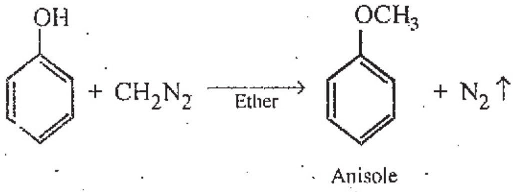
Phenol Benzene

(iii) Alkylation :

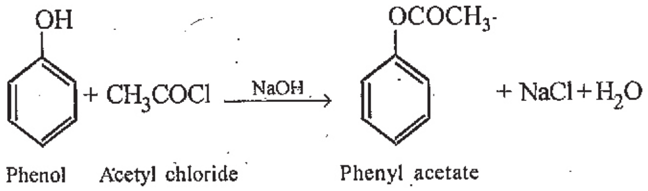
(a) Phenol is alkylated to give Phenolic ethers in the presence of alkali with alkyl halides, for example



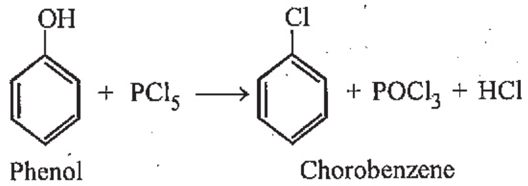
(b) Phenol can be methylated by treatment with diazomethane.



(iv) Acylation :



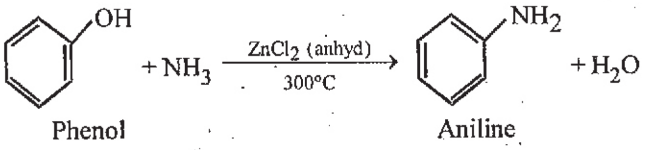
(v) Reaciton with PCl_5 :



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

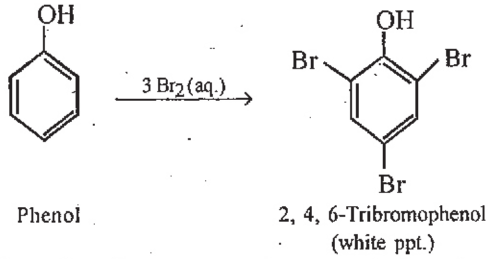
(Triphenylphosphate)

(vi) Reaction with NH_3 : Aniline is obtained



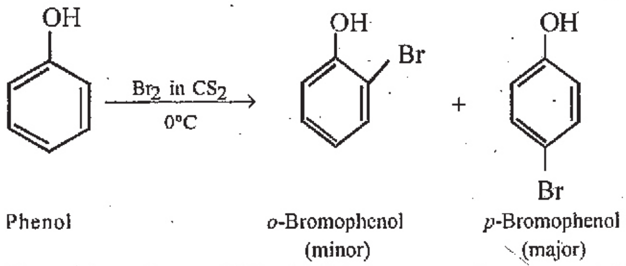
3. Reactions of benzene ring

(i) Halogenation :

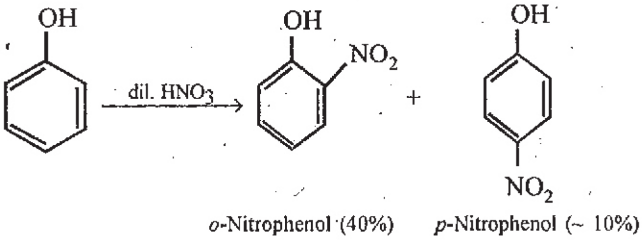


In fact, phenols are so reactive towards bromine water that even substituent like $-SO_3H$, $-NO_2$, $-COOH$, etc. if present, in *o*-and *p*-positions, may be replaced by halogens.

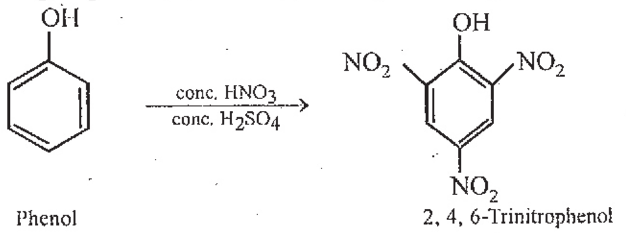
halogenation is carried out at low temperature and in non-polar solvents such as carbon tetrachloride or carbon disulphide. For example,



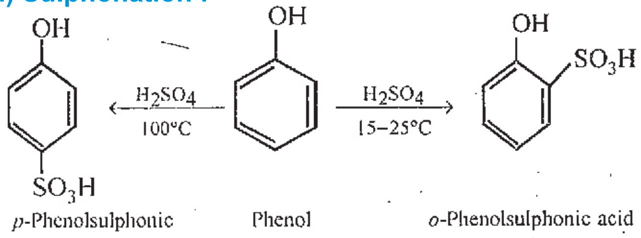
Non-polar solvents (CS_2, CCl_4) decreases the electrophilic character of Br_2 and minimizes ionization of phenol.



Nitration of phenol with concentrated nitric acid or a nitrating reagent gives 2, 4, 6-trinitrophenol (picric acid).

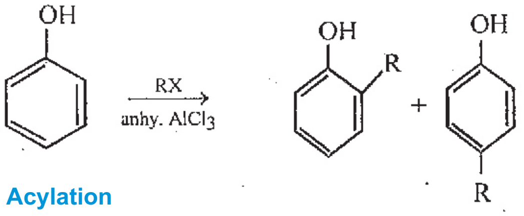


(iii) Sulphonation :

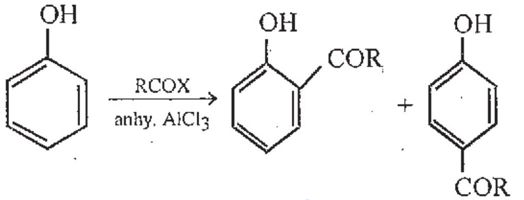


(iv) Friedel - Craft's alkylation and acylation :

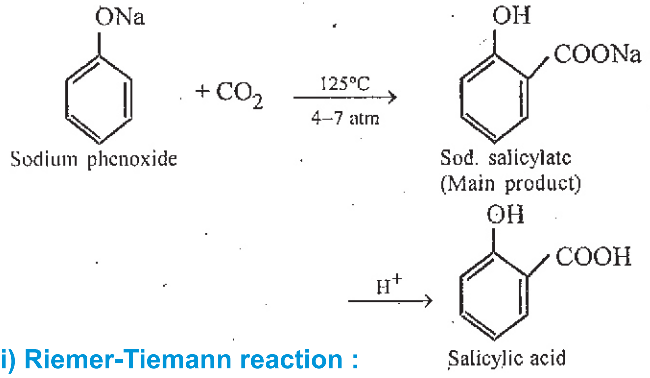
(i) Alkylation



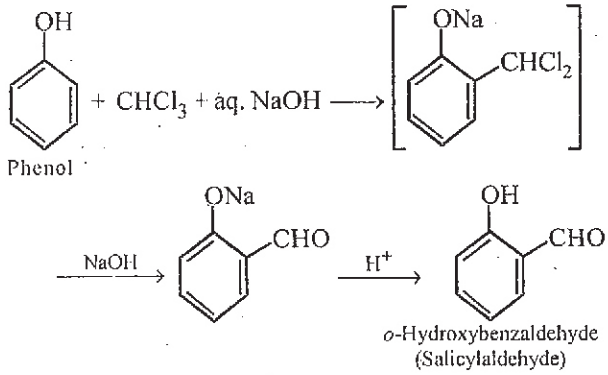
(ii) Acylation

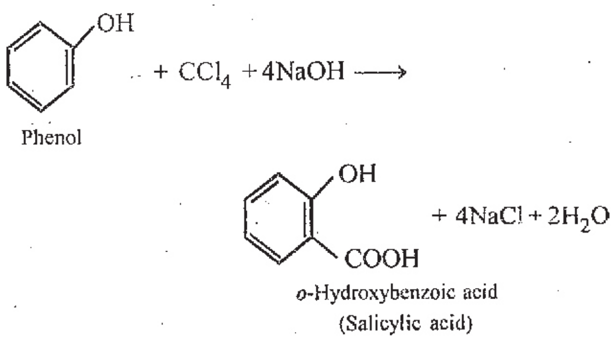


(v) Kolbe's reaction or Kolbe-Schmidt reaction :



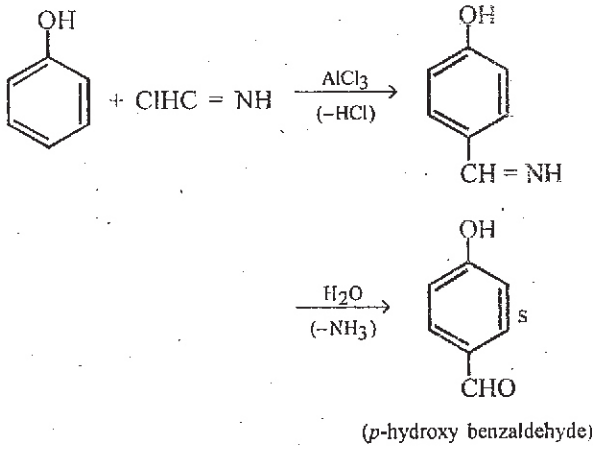
(vi) Riemer-Tiemann reaction :



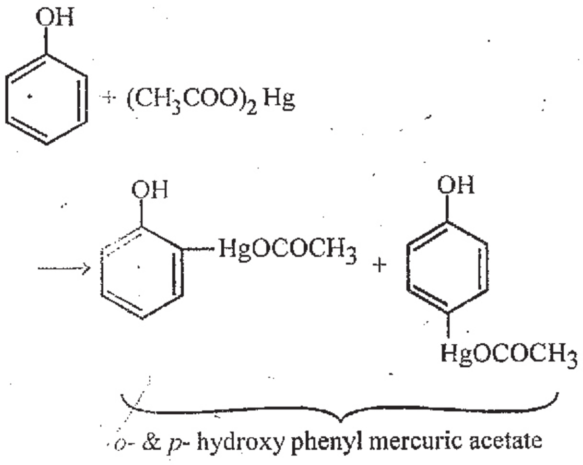


(vii) Gattermann's reaction :

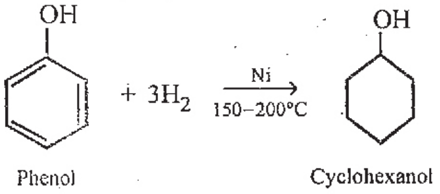
$HCl + H-C\equiv N \xrightarrow{AlCl_3} Cl-HC=NH$



(viii) Mercuration :

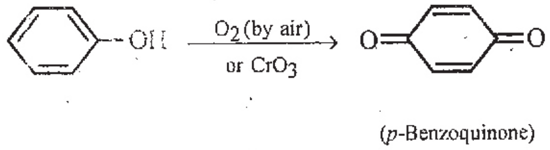


(ix) Hydrogenation :

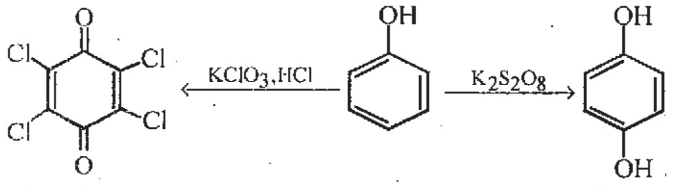


4. Oxidation

(i)



Oxidation by other oxidants :



Tetrachlorquinone
(Chloranil)

(Quinol)

Tests :

(i) Phenol + $FeCl_3$ [neutral] ⟶ Violet colour
(ii) . Bromine water + phenol ⟶ white precipitate
(iii) Blue litmus + phenol ⟶ red
(iv) **Libermann's nitroso test :**

Phenol $\xrightarrow[\text{conc. } H_2SO_4]{NaNO_2}$ Green colouration $\xrightarrow{H_2O}$

Red colouration $\xrightarrow{NaOH}$ Blue colouration

ETHERS

Methods of Preparation

1. By dehydration of alcohols :

$CH_3—CH_2—OH + \text{conc. } H_2SO_4$
Ethanol

$\xrightarrow{100°} CH_3-CH_2-OSO_3H + H_2O$
Ethyl hydrogen sulphate

$CH_3—CH_2—\boxed{OSO_3H + H}—O—CH_2—CH_3$

$\xrightarrow{140°} CH_3–CH_2–O–CH_2–CH_3 + H_2SO_4$
ether

2. Williamson's synthesis : When ethyl halide reacts with sodium ethoxide then ether is formed. Mechanism of the reaction is based on Nucleophilic Substitution.

$R-\boxed{X + Na}OR \longrightarrow R-O-R + NaX$

$CH_3—CH_2—\boxed{I + Na}—O—CH_2—CH_3 \longrightarrow$
Ethyl Iodide Sodium ethoxide

$CH_3–CH_2–O–CH_2–CH_3 + NaI$

3.By reaction of ethyl halide with Ag_2O

$CH_2—CH_2—\boxed{I + Ag}—O—\boxed{Ag + I}—CH_2—CH_3$

$\longrightarrow CH_3–CH_2–O–CH_2–CH_3 + 2AgI$

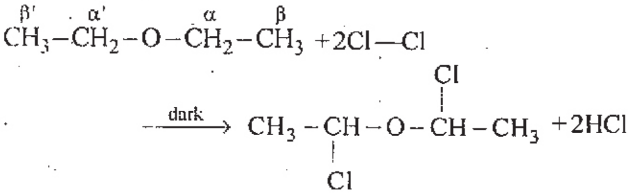
4. By action of diazomethane on alcohols :

$CH_3CH_2OH + CH_2N_2 \xrightarrow{HBF_4} CH_3CH_2OCH_3 + N_2$

Properties

1. Halogenation :

(i) In dark : Halogen reacts with ether in dark and substitutes α and α'- hydrogen atoms.



$$\overset{\beta'}{CH_3}-\overset{\alpha'}{CH_2}-O-\overset{\alpha}{CH_2}-\overset{\beta}{CH_3} + 2Cl—Cl \xrightarrow{dark} CH_3-\underset{Cl}{\underset{|}{CH}}-O-\overset{Cl}{\overset{|}{CH}}-CH_3 + 2HCl$$

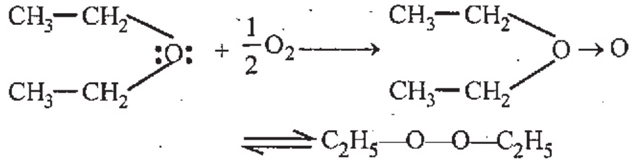
α, α'-Dichlorodiethyl ether

(ii) In light :

$CH_3–CH_2–O–CH_2–CH_3 + 10Cl_2$

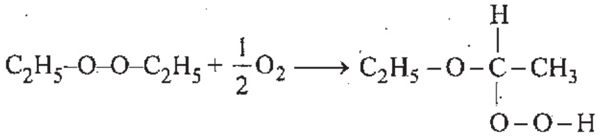
$\xrightarrow{h\nu} CCl_3-CCl_2-O-CCl_2-CCl_3 + 10HCl$
Perchlorodiethyl ether

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



ether peroxide

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



$$C_2H_5-O-O-C_2H_5 + \frac{1}{2}O_2 \longrightarrow C_2H_5-O-\underset{O-O-H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-CH_3$$

Ethoxyethyl hydroperoxide

3. Reaction with HX :

(a) If HX is cold :

$CH_3-O-CH_2-CH_3 + HX(\text{cold}) \longrightarrow CH_3-X + C_2H_5OH$

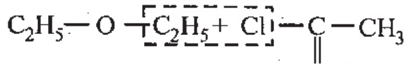
(b) If HX is hot :

$CH_3–CH_2–O–CH_2–CH_3 + 2H–X \xrightarrow{\Delta} 2CH_3–CH_2–X + H_2O$

$CH_3–O–CH_2–CH_3 + 2H–X \xrightarrow{\Delta} CH_3–X + C_2H_5X + H_2O$

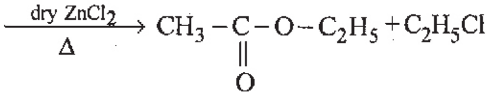
$C_2H_5-O-C_2H_5 + PCl_5 \longrightarrow 2C_2H_5Cl + POCl_3$

4. Reaction with PCl_5 :



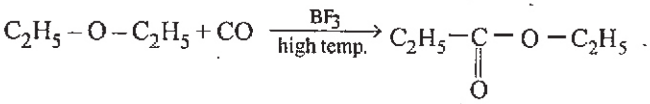
$$C_2H_5—O—\boxed{C_2H_5 + Cl}—\underset{O}{\underset{\|}{C}}—CH_3$$

5. Reaction with Acetyl Chloride :



$$\xrightarrow[\Delta]{\text{dry } ZnCl_2} CH_3-\underset{O}{\underset{\|}{C}}-O-C_2H_5 + C_2H_5Cl$$

6. Reaction with carbon monoxide (carbonylation) :



$$C_2H_5-O-C_2H_5 + CO \xrightarrow[\text{high temp.}]{BF_3} C_2H_5-\underset{O}{\underset{\|}{C}}-O-C_2H_5$$

7. Reduction :

$C_2H_5-O-C_2H_5 + 2H \xrightarrow{Na/liq.\,NH_3} C_2H_6 + C_2H_5-OH$

8. Reaction with H_2SO_4?

(a) With conc. H_2SO_4

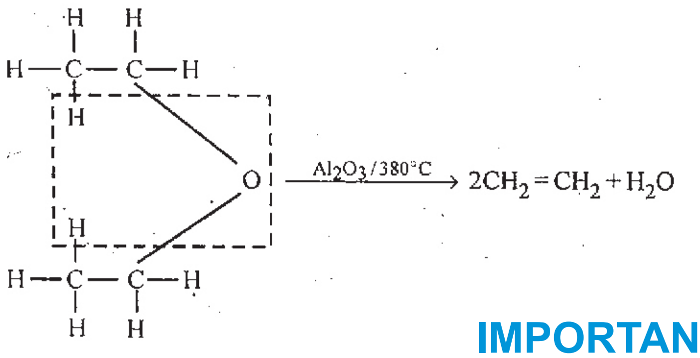
$C_2H_5—O—C_2H_5 + H_2SO_4 \xrightarrow{\Delta} C_2H_5OSO_2OH + C_2H_5OH$
Ethyl hydrogen sulphate

(b) With dil. H_2SO_4 :

$C_2H_5-O-C_2H_5 + H-OH \xrightarrow{dil.\,H_2SO_4} 2C_2H_5OH$

9. Dehydration :

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



Uses

1. Wurtz reaction
2. Alcohol + ether → Natelite (Used in place of petrol)
3. Due to inertness of oxygen, it is best solvent for preparation of highly reactive compounds such as Grignard Reagent.
4. It is used as an anaesthetic.

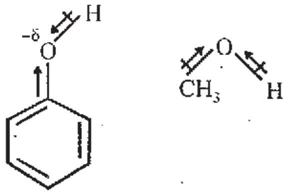
IMPORTANT POINTS

1. Rectified spirit — [95.5% ethanol + 4.5% water] (an example of azeotropic solution)
2. Absolute alcohol — [100% ethanol]
3. Power alcohol — [ethanol + benzene + petrol]
4. Methylated spirit — [rectified spirit + 0.5 % methanol]
5. Denatured spirit — [rectified spirit + pyridine]
6. Wash — [10% to 12% alcohol]
7. Grain spirit — [ethyl alcohol]
8. Raw spirit — [90% alcohol]
9. Wood spirit — [methanol]
10. Boiling point of methanol is 65°C and of ethanol is 78.3°C.
11. Ternary mixutre — Ethanol + Benzene + Water (boiling point 65°C)
12. Binary mixture — Benzene + Ethanol (boiling point 68°C)

Miscellaneous Solved Examples

Example 1 : Phenol has a smaller dipole moment than methanol. Explain.

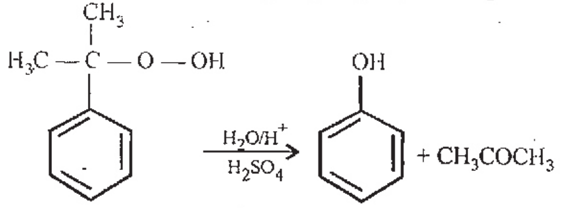
Sol. It is due to the electron withdrawing nature of benzene ring attached to oxygen atom in phenol and electron repelling nature of methyl group attached to oxygen atom is methanol. The difference in electronegativity of Sp^2–C & oxygen in phenol is less than that is Sp^3–C & oxygen in methanol.



Example 2 : Write equations when
(a) thionyl chloride acts upon 1-propanol.
(b) cumene hydroperoxide is treated with dil H_2SO_4.

Sol. (a) $CH_3CH_2CH_2OH + SOCl_2 \xrightarrow{\Delta} CH_3CH_2CH_2CH_2Cl + SO_2 + HCl$

(b)

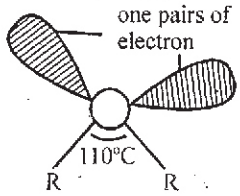


Example 3 : Why phenol is more easily nitrated than benzene?

Sol. Nitration involves an attack of nitronium ion, NO_2^+ (electrophilic) on benzene ring. The –OH group is electron donating and its presence increases the electron density on benzene ring (+ I effect). Therefore, phenol is easily nitrated as compared to benzene.

Example 4 : An ether would possess a dipole moment even if alkyl groups present in it are identical. Explain.

Sol. It is because of angular structure of C — O — C bond (like H — O — H bond is water). In structure of ether, C — O — C bond is about 110°. The dipoles are towards lone pairs of electrons which increase the dipole moment.



Example 5 : Why are Grignard reagents soluble in ether but not in benzene?

Sol. Grignard reagents form coordination complexes with ethers but not with benzene since the former has lone pairs of electrons but the latter does not.

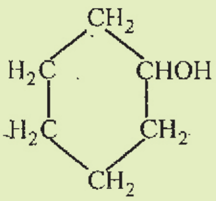
dpp

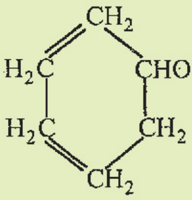
Daily **Practice** Problems

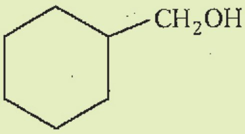
TARGET : IIT-JEE / NEET

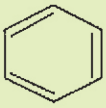
1. How many isomers of $C_5H_{11}OH$ will be primary alcohols ?
(a) 5 (b) 4 (c) 2 (d) 3

2. The structural formula of cyclohexanol is

(a)


(b)


(c)


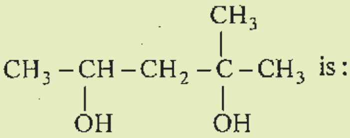
(d)


3. Molecular formula of amyl alcohol is
(a) $C_7H_{14}O$ (b) $C_6H_{13}O$ (c) $C_5H_{12}O$ (d) $C_5H_{10}O$

4. Carbolic acid is
(a) phenol (b) phenyl benzoate
(c) phenyl acetate (d) salol

5. Which of the following is dihydric alcohol ?
(a) Glycerol (b) Ethylene glycol
(c) Catechol (d) Resorcinol

6. The IUPAC name of



$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_3$$

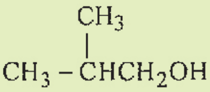
is :
(a) 1, 1-dimethyl-1, 3-butanediol
(b) 2-methyl-2, 4-pentanediol
(c) 4-methyl-2, 4-pentanediol
(d) 1, 3; 3-trimethyl-1, 3-propanediol

7. HBr reacts fastest with
(a) 2-Methylpropan-1-ol (b) 2-Methylpropan-2-ol
(c) propan-2-ol (d) propan-1-ol.

8. Which one of the following on oxidation gives a ketone ?
(a) Primary alcohol (b) Secondary alcohol
(c) Tertiary alcohol (d) All of these

9. *n*-Propyl alcohol and isopropyl alcohol can be chemically distinguished by which reagent?
(a) PCl_5
(b) Reduction
(c) Oxidation with potassium dichromate
(d) Ozonolysis

10. Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is

(a)


$CH_3-\overset{CH_3}{\overset{|}{C}}HCH_2OH$

(b) $PhCHOHCH_3$
(c) $CH_3CH_2CH(OH)CH_2CH_3$ (d) $C_6H_5CH_2CH_2OH$

11. The best method to prepare cyclohexene from cyclohexanol is by using
(a) Conc. $HCl + ZnCl_2$ (b) Conc. H_3PO_4
(c) HBr (d) Conc. HCl

12. $C_6H_5-CH=CHCHO \xrightarrow{X} C_6H_5CH=CHCH_2OH$. In the above sequence X can be
(a) H_2/Ni (b) $NaBH_4$
(c) $K_2Cr_2O_7/H^+$ (d) Both (a) and (b)

13. Acid catalyzed hydration of alkenes except ethene leads to the formation of
(a) primary alcohol
(b) secondary or tertiary alcohol
(c) mixture of primary and secondary alcohols
(d) mixture of secondary and tertiary alcohols

14. Which one of the following is not formed when glycerol reacts with HI ?
(a) $CH_3-CHI-CH_3$ (b) $CH_3-CH=CH_2$
(c) $CH_2OH-CHI-CH_2OH$ (d) $CH_2=CH-CH_2I$

15. Which of the following reagent is best to change glycerol to acrolein ?
(a) P_2O_5 (b) Conc. H_2SO_4
(c) Anhydrous $CaCl_2$ (d) $KHSO_4$

16. Which one of the following alcohols is least soluble in water?
(a) CH_3OH (b) C_3H_7OH
(c) C_4H_9OH (d) $C_{10}H_{21}OH$

17. Lucas test is done to differentiate between :
(a) alcohol and ketone
(b) alcohol and aromatic ketones
(c) 1°, 2° and 3° alcohols
(d) None of these

18. The dehydration of 2-methylbutanol with conc. H_2SO_4 gives :
(a) 2-Methylbutene as major product
(b) Pentene
(c) 2-Methylbut-2-ene as major product
(d) 2-Methylpent-2-ene

19. Which of the following will not give a positive iodoform test?
(a) $CH_3CH_2CHOHCH_3$ (b) $CH_3CH_2CH_2COCH_3$
(c) $CH_3CH_2COCH_2CH_3$ (d) $CH_3COC_6H_5$

20. In the reaction :

$$A \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \text{acetone} \xrightarrow{\text{oxidation}} \text{acetic acid}$$

A is
(a) 1- propanol (b) 2-butanol
(c) 2-propanol (d) ethanol

21. In the reaction :

$CH_3OH \xrightarrow{\text{oxidation}} A \xrightarrow{NH_3} B$; A and B respectively are

(a) $HCHO, HCOONH_4$ (b) $HCOOH, HCOONH_4$

(c) $HCOOH, HCONH_2$ (d) $HCHO, HCONH_2$

22. Glycerol is more viscous than ethanol due to

(a) high molecular weight

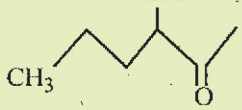
(b) high boiling point

(c) many hydrogen bonds per molecule

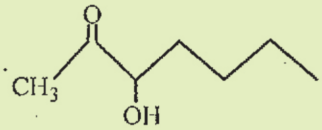
(d) Fajan's rule

23. Which one of the following compounds will be most readily dehydrated?

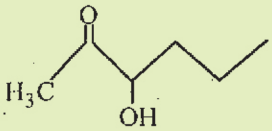
(a)



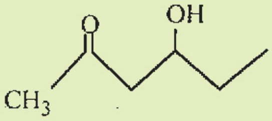
(b)



(c)



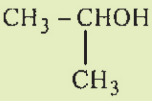
(d)



24. Following compounds are given:

(i) CH_3CH_2OH (ii) CH_3COCH_3

(iii)



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CHOH}}$

(iv) CH_3OH

Which of the above compound(s), on being warmed with iodine solution and NaOH, will give iodoform?

(a) (i) and (ii) (b) (i), (iii) and (iv)

(c) only (i) (d) (i), (ii) and (iii)

25. Which one of the following compounds will be most readily attacked by an electrophile ?

(a) Chlorobenzene (b) Benzene

(c) Phenol (d) Toluene

26. When phenol is heated with $CHCl_3$ and NaOH then salicylaldehyde is produced. This reaction is known as

(a) Rosenmund's reaction (b) Reimer-Tiemann reaction

(c) Friedel-Crafts reaction (d) Sommelet reaction

27. When phenol is treated with excess bromine water. It gives

(a) *m*-Bromophenol (b) *o*-and *p*-Bromophenols

(c) 2,4-Dibromophenol (d) 2,4, 6-Tribromophenol.

28. Which is formed when benzalamine react with nitrous acid

(a) C_6H_5OH (b) C_6H_5ON

(c) $C_6H_5N_2OH$ (d) $C_6H_5CH_2OH$

29. Benzyl alcohol is obtained from benzaldehyde by:

(a) Perkin's reaction (b) Wurtz reaction

(c) Cannizzaro's reaction (d) Claisen's reaction

30. On distillation with Zn dust, phenol gives :

(a) acetophenone (b) benzoic acid

(c) benzene (d) benzophenone

31. To distinguish between salicylic acid and phenol, one can use :

(a) $NaHCO_3$ solution (b) 5% NaOH solution

(c) neutral $FeCl_3$ (d) bromine water

32. Which one is formed when sodium phenoxide is heated with ethyl iodide ?

(a) Phenetole (b) Ethyl phenyl alcohol

(c) Phenol (d) None of these

33. In Williamson's synthesis, ethoxyethane is prepared by

(a) passing ethanol over heated alumina

(b) sodium ethoxide with ethyl bromide

(c) ethyl alcohol with sulphuric acid

(d) ethyl iodide and dry silver oxide

34. The reaction of sodium ethoxide with ethyl iodide to form diethyl ether is termed

(a) electrophilic substitution (b) nucleophilic substitution

(c) electrophilic addition (d) radical substitution

35. Which of the following product is formed, when ether is exposed to air ?

(a) Oxide (b) Alkanes

(c) Alkenes (d) Peroxide of diethyl ether

36. In the following reaction

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

(a) ethane (b) ethylene (c) butane (d) propane

37. The ether that undergoes electrophilic substitution reactions is

(a) $CH_3OC_2H_5$ (b) $C_6H_5OCH_3$

(c) CH_3OCH_3 (d) $C_2H_5OC_2H_5$

38. An ether is more volatile than an alcohol having the same molecular formula. This is due to

(a) dipolar character of ethers

(b) alcohols having resonance structures

(c) inter-molecular hydrogen bonding in ethers

(d) inter-molecular hydrogen bonding in alcohols

39. Diethyl ether on heating with conc. HI gives two moles of

(a) ethanol (b) iodoform

(c) ethyl iodide (d) methyl iodide

40. Methylphenyl ether can be obtained by reacting

(a) phenolate ions and methyl iodide

(b) methoxide ions and bromobenzene

(c) methanol and phenol

(d) bromo benzene and methyl bromide

41. The cleavage of an aryl-alkyl ether with cold HI gives :

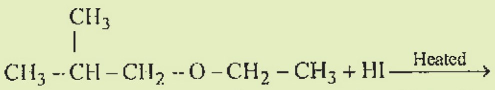
(a) alkyl iodide and water

(b) aryl iodide and water

(c) alkyl iodide, aryl iodide and water

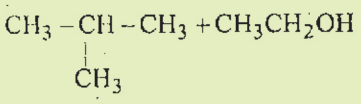
(d) phenol and alkyl iodide

42. In the reaction:

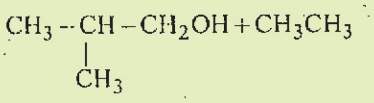


$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CH_2-O-CH_2-CH_3+HI\xrightarrow{\text{Heated}}$$

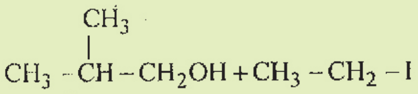
Which of the following compounds will be formed?

(a) 

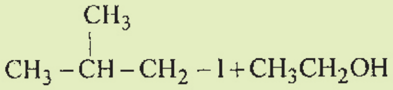
$$CH_3-\underset{CH_3}{\underset{|}{C}H}-CH_3+CH_3CH_2OH$$

(b) 

$$CH_3-\underset{CH_3}{\underset{|}{C}H}-CH_2OH+CH_3CH_3$$

(c) 

$$CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2OH+CH_3-CH_2-I$$

(d) 

$$CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-I+CH_3CH_2OH$$

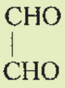
43. Consider the following reaction;

ethanol $\xrightarrow{PBr_3}$ X $\xrightarrow{alc.KOH}$ Y $\xrightarrow[\text{(ii) } H_2O\text{, heat}]{\text{(i) } H_2SO_4\text{ room temperature}}$ Z;

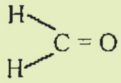
the product Z is:

(a) $CH_3CH_2-O-CH_2-CH_3$ (b) $CH_3-CH_2-O-SO_3H$
(c) CH_3CH_2OH (d) $CH_2=CH_2$

44. $H_2COH\cdot CH_2OH$ on heating with periodic acid gives:

(a) 2HCOOH (b) 

$$\underset{CHO}{\overset{CHO}{|}}$$

(c) 2 

$$H_2C=O$$

(d) $2CO_2$

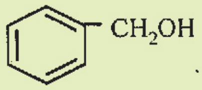
45. Consider the following reaction:

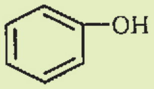
Phenol $\xrightarrow{\text{Zn dust}}$ X $\xrightarrow[\text{Anhydrous } AlCl_3]{CH_3Cl}$ Y $\xrightarrow{\text{Alkaline } KMnO_4}$ Z

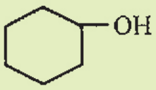
The product Z is:

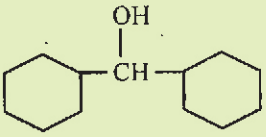
(a) benzaldehyde (b) benzoic acid
(c) benzene (d) toluene

46. Which one of the following compounds has the most acidic nature?

(a) 

(b) 

(c) 

(d) 

47. Among the following four compounds

(i) phenol (ii) methylphenol
(iii) meta-nitrophenol (iv) para-nitrophenol

the acidity order is :

(a) ii > i > iii > iv (b) iv > iii > i > ii
(c) iii > iv > i > ii (d) i > iv > iii > ii

48. When glycerol is treated with excess of HI, it produces:

(a) glycerol triiodide (b) 2–iodopropane
(c) allyl iodide (d) propene

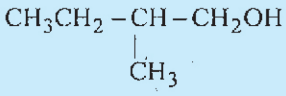
49. Which of the following compounds can be used as antifreeze in automobile radiators ?

(a) Methyl alcohol (b) Glycol
(c) Nitrophenol (d) Ethyl alcohol

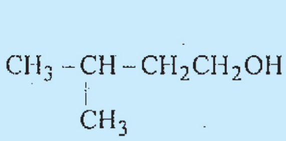
SOLUTION

1. **(b)** Four primary alcohols of $C_5H_{11}OH$ are possible. These are:

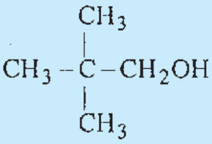
(i) $CH_3CH_2CH_2CH_2CH_2OH$

(ii)


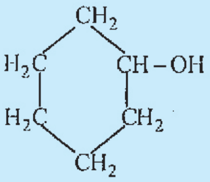
$CH_3CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2OH$

(iii)


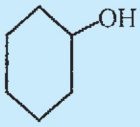
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2CH_2OH$

(iv)


$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2OH$

2. **(a)**


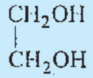
or



3. **(c)**

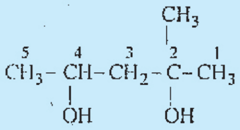
4. **(a)** 5% aqueous solution of phenol at room temperature is called as carbolic acid.

5. **(b)** Glycols are dihydric alcohols (having two hydroxyl groups). Ethylene glycol is the first member of this series.



$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$

(Ethylene glycol)

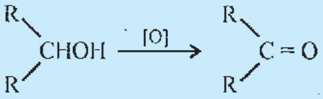
6. **(b)**


$\overset{5}{C}H_3-\overset{4}{C}H(OH)-\overset{3}{C}H_2-\overset{2}{C}(CH_3)(OH)-\overset{1}{C}H_3$

2-methyl- 2, 4-pentanediol.

7. **(b)** Greater the stability of the intermediate carbocation, more reactive is the alcohol. Since 2-methylpropan-2-ol generates 3° carbocation, therefore, it reacts fastest with HBr.

8. **(b)** Secondary alcohols on oxidation give ketones.
Note : – Primary alcohols form aldehydes.



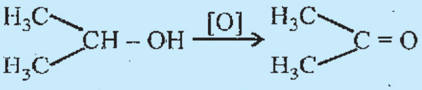
$R_2CHOH \xrightarrow{[O]} R_2C=O$

Isopropyl alcohol Ketone

9. **(c)** Primary alcohol on oxidation give aldehyde which on further oxidation give carboxylic acid whereas secondary alcohols give ketone.

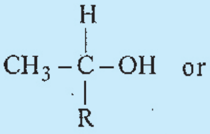
$CH_3CH_2CH_2OH \xrightarrow{[O]}$
n-propyl alcohol

$CH_3CH_2CHO \xrightarrow{[O]} CH_3CH_2COOH$

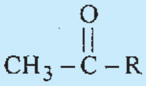


$(H_3C)_2CH-OH \xrightarrow{[O]} (H_3C)_2C=O$

isopropyl alcohol Ketone

10. **(b)** The compounds containing


$CH_3-\overset{H}{\overset{|}{\underset{R}{\underset{|}{C}}}}-OH$ or



$CH_3-\overset{O}{\overset{||}{C}}-R$ (R = H, alkyl or aryl) give CHI_3 with I_2 and NaOH.

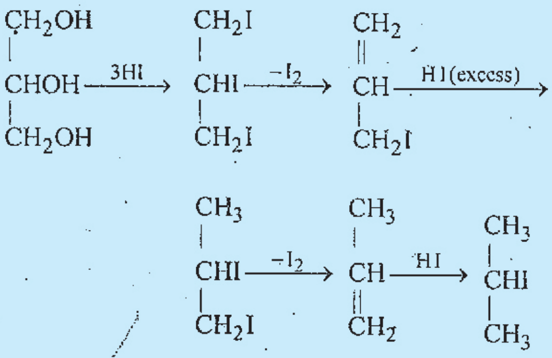
11. **(b)** Conc. HCl, HBr and conc. HCl + $ZnCl_2$ all are nucleophiles, thus convert alcohols to alkyl halides. However, conc. H_3PO_4 is a good dehydrating agent which converts an alcohol to an alkene.

12. **(b)** $NaBH_4$ and $LiAlH_4$ attacks only carbonyl group and reduce it into alcohol group.

$C_6H_5-CH=CHCHO \xrightarrow{NaBH_4}$
cinnamic aldehyde

$C_6H_5-CH=CH.CH_2OH$
cinnamic alcohol

13. **(b)**

14. **(c)**


$CH_2OH-CHOH-CH_2OH \xrightarrow{3HI} CH_2I-CHI-CH_2I \xrightarrow{-I_2} CH_2=CH-CH_2I \xrightarrow{HI(excess)}$

$CH_3-CHI-CH_2I \xrightarrow{-I_2} CH_3-CH=CH_2 \xrightarrow{HI} CH_3-CHI-CH_3$

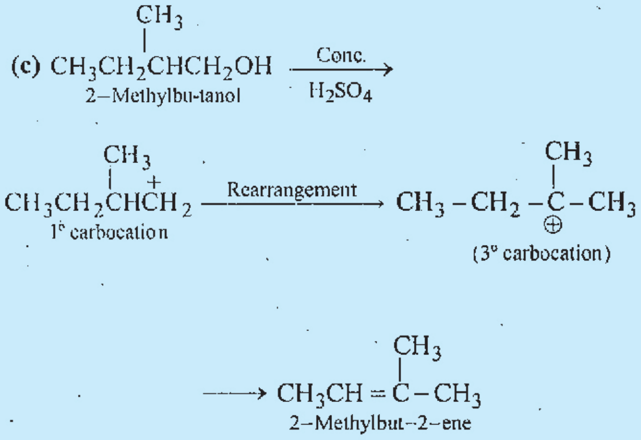
∴ All the compounds except (C), $CH_2OH-CHI-CH_2OH$ are formed during reaction of glycerol with excess HI.

15. **(d)** Glycerol is dehydrated by using dehydrating agent like P_2O_5 or conc H_2SO_4 or $KHSO_4$ but $KHSO_4$ is best of them.

16. **(d)** Solubility of alcohol in water decreases with increase in molecular mass due to increase in water repelling alkyl part in alcohol.

17. **(c)** Lucas test is used to distinguish between 1°, 2° and 3° alcohols. Lucas reagent is anhy. $ZnCl_2$ and HCl.
3° alcohol + Lucas reagent ⟶ turbidity immediately
2° alcohol + Lucas reagent ⟶ turbidity after 5 minutes
1° alcohol + Luces reagent ⟶ No turbidity at room temperature.

18. (c)



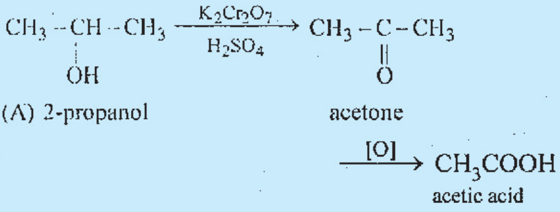
$$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2OH \xrightarrow[H_2SO_4]{Conc.}$$
2–Methylbutanol

$$CH_3CH_2\overset{\overset{CH_3}{|}}{C}H\overset{+}{C}H_2 \xrightarrow{Rearrangement} CH_3-CH_2-\underset{\oplus}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$
1° carbocation (3° carbocation)

$$\longrightarrow CH_3CH=\overset{\overset{CH_3}{|}}{C}-CH_3$$
2–Methylbut–2–ene

19. (c) $CH_3CH_2COCH_2CH_3$ has neither $-COCH_3$ nor $-CHOHCH_3$, it does not undergo iodoform test.

20. (c)



$$\underset{\underset{OH}{|}}{CH_3-CH-CH_3} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\underset{\underset{O}{||}}{C}-CH_3 \xrightarrow{[O]} CH_3COOH$$
(A) 2-propanol acetone acetic acid

21. (b) $CH_3OH \xrightarrow{Oxidation} \underset{(A)}{HCOOH} \xrightarrow{NH_3} \underset{(B)}{HCOONH_4}$

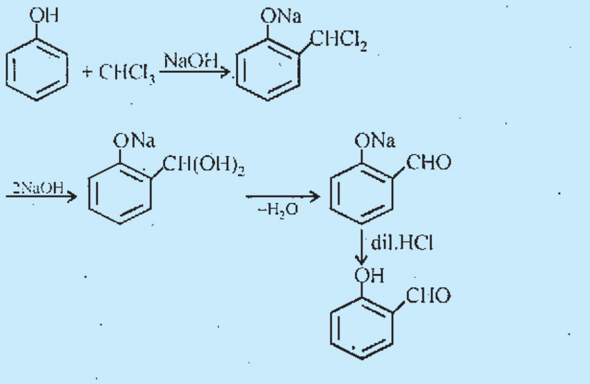
22. (c) Because of larger (three per molecule) number of intermolecular hydrogen bonding in case of glycerol ($CH_2OH-CHOH-CH_2OH$) as compared to ethanol (CH_3CH_2OH), the attraction between molecules of glycerol is more than that of molecules of ethanol. Due to this glycerol is more viscous than ethanol.

23. (d) The intermediate is carbocation which is destabilised by $C=O$ group (present on α-carbon to the –OH group) in the first three cases. In (d), α–hydrogen is more acidic which can be removed as water. Moreover, the positive charge on the intermediate carbocation is relatively away from the $C=O$ group.

24. (d) Among the given compounds only CH_3OH does not give iodoform reaction.

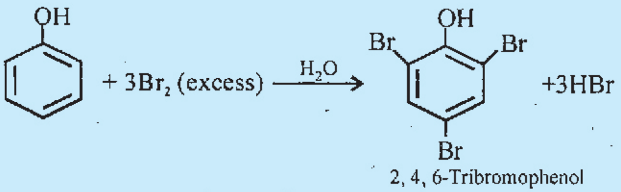
25. (c) Due to strong electron-donating effect of the OH group, the electron density in phenol is much higher than that in toluene, benzene and chlorobenzene and hence phenol is readily attacked by the electrophile.

26. (b)

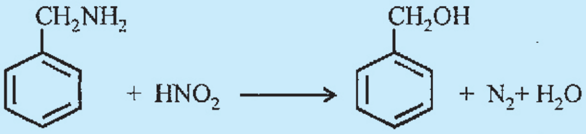


Reimer-Tiemann reaction.

27. (d) With Br_2 water, phenol gives 2, 4, 6- tribromophenol.



28. (d)



29. (c) **Perkin reaction** involves reaction of aromatic aldehyde with aliphatic acid anhydride in presence of sodium salt of the same acid as anhydride to form α, β-unsaturated acid.

$$C_6H_5CHO+(CH_3CO)_2O \xrightarrow{CH_3COONa} C_6H_5CH=CHCOOH+CH_3COOH$$

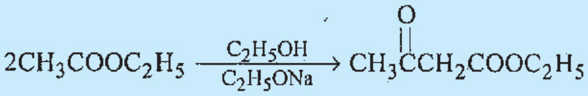
Wurtz reaction involves the reaction of an alkyl halide with metallic sodium in dry ether to form higher hydrocarbon.

$$RX+2Na+XR \xrightarrow[ether]{dry} R-R+2NaX$$

Cannizzaro reaction is given by aldehydes having no α-hydrogen atom to form a mixture of alcohol and sodium salt of the acid. It is a disproportionation reaction in which half of the aldehyde molecules are oxidised and other half reduced in presence of NaOH.

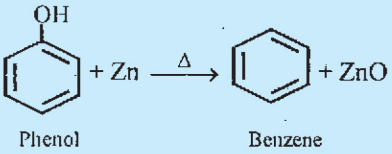
$$2C_6H_5CHO \xrightarrow{NaOH} C_6H_5CH_2OH+C_6H_5COONa$$

Claisen reaction is the self condensation of esters having α-hydrogen atom in presence of strong base to form β-keto ester.

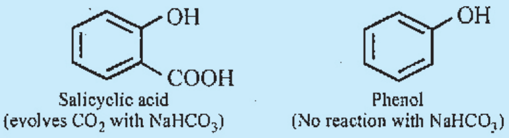


$$2CH_3COOC_2H_5 \xrightarrow[C_2H_5ONa]{C_2H_5OH} CH_3\overset{\overset{O}{||}}{C}CH_2COOC_2H_5$$

30. (c)



31. (a)



32. (a) $C_6H_5ONa+C_2H_5I \xrightarrow{\Delta} \underset{Phenetole}{C_6H_5OC_2H_5}+NaI$

33. (b) Williamson's synthesis -

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

34. (b) Reaction of sodium ethoxide with ethyl iodide to produce diethyl ether is known as Williamson synthesis.
It is a nucleophilic substitution reaction and proceeds via S_N2 mechanism.

35. (d) $C_2H_5-O-C_2H_5+O_2 \xrightarrow[25°C]{hv} CH_3-CH(OOH)-O-C_2H_5$

36. (a) $C_2H_5OC_2H_5 \xrightarrow[\text{Cleavage of ethers}]{\text{Red P / HI}} 2C_2H_5I \xrightarrow[\text{Reduction}]{\text{Red P / HI}} \underset{\text{Ethane}}{2C_2H_6}$

37. (b) Only alkyl aryl ethers e.g., $C_6H_5OCH_3$ undergoes electrophilic substitution reactions.

38. (d) Due to inter-molecular hydrogen bonding in alcohols boiling point of alcohols is much higher than ether.

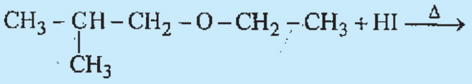
39. (c) $C_2H_5OC_2H_5+2\,HI \xrightarrow{\Delta} 2\,C_2H_5I+H_2O$

40. (a) $C_6H_6O^-+CH_3I \rightarrow C_6H_5OCH_3+I^-$

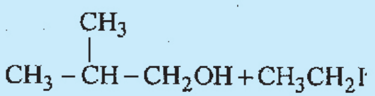
41. (d) $\underset{\text{Aryl-alkyl ether}}{R-O-Ar}+HI \longrightarrow \underset{\text{Phenol}}{Ar-OH} + \underset{\text{Alkyl iodide}}{RI}$

Due to steric hinderance, smaller alkyl group is always attached to iodine.

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

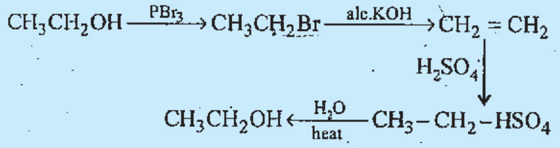


$$\underset{\underset{CH_3}{|}}{CH_3-CH}-CH_2-O-CH_2-CH_3+HI \xrightarrow{\Delta}$$



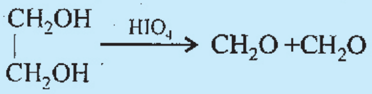
$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2OH+CH_3CH_2I$$

43. (c)



$$\begin{tikzcd} CH_3CH_2OH \arrow[r, "PBr_3"] & CH_3CH_2Br \arrow[r, "alc.KOH"] & CH_2=CH_2 \arrow[d, "H_2SO_4"'] \\ & CH_3CH_2OH & CH_3-CH_2-HSO_4 \arrow[l, "H_2O"', "heat"] \end{tikzcd}$$

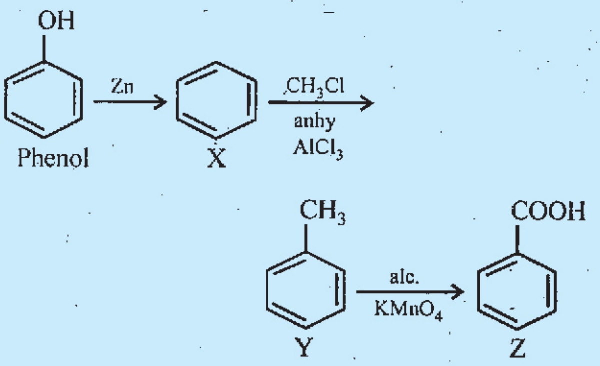
44. (c) 1, 2 – Diols, when treated with an aqueous solution of periodic acid give aldehyde



$$\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix} \xrightarrow{HIO_4} CH_2O+CH_2O$$

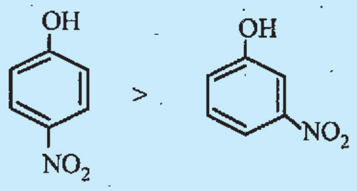
Note that a 1° alcohol gives CH_2O. Since in glycol both the OH groups, are primary hence give 2 molecules of CH_2O as by product.

45. (b)



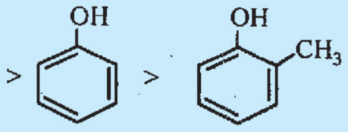
46. (b) Phenol is most acidic because its conjugate base is stabilised due to resonance, while the rest three compounds are alcohols, hence, their corrosponding conjugate bases do not exhibit resonance

47. (b)



(iv) (iii)

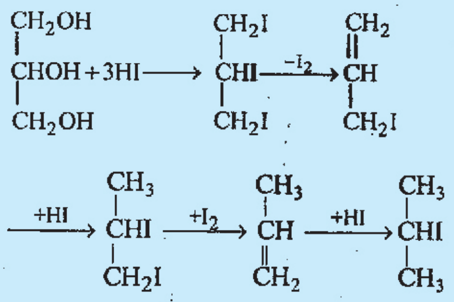
(– I and – M effects, both increase acidity) (only – I effect)



(i) (ii)

(+ I effect of CH_3 group decreases acidity)

48. (b) Glycerol when treated with excess HI produces 2–iodopropane



49. (b) Glycol is used as an antifreeze in automobiles.