

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

$$\begin{array}{c} C_2H_5Br + KOH \to C_2H_5OH + KBr \\ \text{Bromoethan e} & \text{Ethanol} \\ \\ C_2H_5Br + AgOH \to C_2H_5OH + AgBr \\ \text{Bromoethan e} & \text{Moist silver oxide} \\ \end{array}$$

- □ 1° alkyl halide gives good yield of alcohols.
- $\ \square$ 2° alkyl halide gives mixture of alcohol and alkene.
- $\ \square$ 3° alkyl halide gives alkenes due to dehydrohalogenation.

$$CH_{3} \qquad CH_{3}$$

$$CH_{3} - C - CH_{3} + KOH \rightarrow CH_{3} - C = CH_{2}$$

$$Br \qquad (Aqueous) \qquad 2-Methy | propene \\ (Major product)$$

$$CH_{3} + CH_{3} - C - CH_{3} + KBr + H_{2}O$$

$$OH$$
Tert but 1 alcohol(side product)

(ii) From alkenes: (a) Hydration

Indirect process:

$$CH_2 = CH_2 + HOSO_2OH \rightarrow CH_3CH_2OSO_2OH$$
 Ethene Sulphuric acid Ethyl hydrogen sulphate
$$\frac{H_2O}{\text{Boil}} \rightarrow CH_3CH_2OH + H_2SO_4$$
 Ethanol

In case of unsymmetrical alkenes

$$CH_{3}CH = CH_{2} + HOSO_{2}OH \xrightarrow{\text{Markowniko ff's} \\ \text{rule}}$$

$$CH_{3} - CH - CH_{3} \xrightarrow{\text{H}_{2}O} CH_{3} - CH - CH \\ OSO_{2}OH \xrightarrow{\text{Boil}} CH_{3} - CH - CH \\ OH_{2}OH_{2}OH \xrightarrow{\text{Propan-2-ol}} CH_{3} \xrightarrow{\text{CH}_{3}} CH_{3} CH_{$$

(b) Oxymercuration-demercuration

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)

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

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

$$H B H_2$$
All to be great.

$$(R\ CH_2\ CH_2)_2\ BH \xrightarrow{RCH=CH_2} (RCH_2\ CH_2)_3\ B$$
 Dialky I borane Trialky I borane

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

(iii) By reduction of carbonyl compounds

$$RCHO + H_2 \xrightarrow{Pd} RCH_2OH$$
Aldehyde Primaryalcohol

$$\begin{array}{c}
RCOR' + H_2 \xrightarrow{NaBH_4} R - CH - R' \\
Ni/Pt & OH \\
Secondary alcohol
\end{array}$$

$$CH_{2} = CH_{2} - H_{3}O^{+}CH_{3} - H_{2}O CH_{3} + H_{2}O CH_{3} + H_{3}O CH_{3} + H_{4}O CH_{3} + H_{5}O CH_{5}O CH_{5}O$$

LiAlH₄ also reduces epoxides into alcohol:

$$CH_2 - CH_2 + LiAIH_4 \rightarrow CH_3 - CH_2OH$$

Hydride selectively attacks the less alkylated carbon of the epoxide.

$$CH_{3} \xrightarrow{C} CH_{2} \xrightarrow{LiAIH_{4}} CH_{3} \xrightarrow{C} C-CH_{3}$$

$$OH$$

(iv) By reduction of carboxylic acids and their derivatives

$$\begin{array}{c} R-COOH & \xrightarrow{\quad \text{(i) LiAlH }_4 \quad} RCH_2OH \\ \text{Carboxy lic acid} & \text{(ii) } H_2O & \text{primary alcohol} \end{array}$$

$$\begin{array}{c} RCOOH \\ Carboxylic acid \end{array} \rightarrow \begin{array}{c} RCOOR' \xrightarrow{H_2} RCH_2OH + R'OH \end{array}$$

Esters are also reduced to alcohols

(Bouveault Blanc reaction)

$$CH_{3} - C - OCH_{3} + 4[H] \xrightarrow{Na/C_{2}H_{5}OH} CH_{3}CH_{2}OH + CH_{3}OH$$
Methylacetate

(Extract)
Methanol

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

$$Me_2C = O + (CH_3)_2 CHOH$$
Isopropylalcohol

$$Me_2CHOH + \frac{CH_3}{CH_3}C = O$$

(v) By alkaline hydrolysis of ester

$$\begin{array}{ccc}
O & O \\
R - C - O R' + HO Na (aq) \rightarrow R - C - ONa + R'OH \\
Sod. salt of acid Alcohol$$

(vi) From primary amines

$$\begin{array}{c} CH_{3}CH_{2}NH_{2} + HONO \xrightarrow{NaNO_{2}/HCl} \\ \text{Aminoethane} \end{array} \rightarrow$$

$$CH_3CH_2OH + N_2 + H_2O$$

 \Box 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:

$$2R-Mg-X+O_2 \xrightarrow[Al_2O_3]{\Delta} 2R-O-Mg-X \ .$$

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

(b) With ethylene oxide:

$$R^{\delta-} - Mg^{\delta+} - X + \underbrace{CH_2 - CH_2}_{O_{\delta-}} \rightarrow$$

$$RCH_2CH_2 - OMgX \xrightarrow{H_2O} RCH_2CH_2OH + Mg(X)OH$$

(c) With carbonyl compounds:

- \square If R' = H, product will be 1°alcohol.
- \square If R' = R, product will be 2°alcohol.
- $\ \square$ If carbonyl compound is a ketone, product will be 3° alcohol.
- \Box 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.

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

$$CH_{3} - CH - CHO \xrightarrow{H_{2}} CH_{3} - CH - CH_{2}OH$$

$$CH_{3} \qquad CH_{3} \qquad CH_{3}$$

$$(Minor) \qquad Isobutyl alcohol$$

$$CH_{3} - CH_{2} - CH_{2} - CHO \xrightarrow{H_{2}} CH_{2} - C$$

(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 12carbon 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 R R R R

character to OH bond.

(iv) Solubility: The lower alcohols are miscible

$$H - O: \stackrel{\delta^-}{\underset{R}{\overset{\delta^-}{\longrightarrow}}} - \cdots \stackrel{\delta^+}{\underset{H}{\overset{\delta^-}{\longrightarrow}}} H - O: \text{ Solubility } \propto \frac{1}{\text{Size of alkyl groups}}$$

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

Isomeric 1°, 2°, 3° alcohols have solubility in order $1^{\circ} > 2^{\circ} > 3^{\circ}$.

(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 ∞ 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.

$$-\overset{\circ}{\overset{\circ}{\underset{\mid}{\bigcap}}} \overset{\circ}{\underset{\mid}{\bigcap}} \leftarrow H^{\delta +}$$
Polar

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

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.

(a) Reaction with Na: (Active metals)

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

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: $R - O - H + : B^{-} \rightarrow R - O : - + B - H$ Alcohol
> Base
> Alkoxide
> Alkoxide

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

$$\begin{array}{ccc} .. & .. \\ H-O-H+RO^-: \longrightarrow R-O-H & +OH^- \\ .. & .. \\ Acid & Base \end{array}$$

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

(c) Reaction with acid derivatives: (Analytical test

$$CH_3 - C \\ + Cl + H \\ + O - CH_2CH_3$$
 Ethanoyl chloride Ethanol

$$\xrightarrow{\text{Pyridine}} CH_3 - C - OCH_2CH_3 + HCl$$
Ethylethanoate (Ethylacetate)

$$\begin{array}{c|c} O & O \\ \parallel & \parallel \\ \text{Acylation}: CH_3 - C - O - C - CH_3 + H - OCH_2CH_3 \\ \text{Aceticanhy dride} \end{array}$$

$$\begin{array}{c}
O \\
\parallel \\
CH_3 - C - OCH_2CH_3 + CH_3COOH
\end{array}$$
Ethylethanoate

(d) Reaction with grignard reagents:

$$\begin{array}{ccc} CH_3OH + & C_2H_5MgBr & \rightarrow & C_2H_6 + CH_3OMgBr \\ & \text{Methyl} & & \text{Ethane} \\ & \text{alcohol} & & \text{bromide} \end{array}$$

(e) Reaction with ketene:

(f) Reaction with isocyanic acid:

$$R - \overset{\delta-}{O} - \overset{\delta+}{H} + H - N = \overset{\delta+}{C} \xrightarrow{A} H - N = \overset{C}{C} - O - R$$

$$O_{\delta-} \qquad OH$$

$$\rightarrow H - NH - C - O - R$$

$$O$$
amino ester
((Izathana))

(g) Reaction with ethylene oxide:

$$R - O - H + CH_2 - CH_2 \rightarrow CH_2 - CH_2 \xrightarrow{ROH} CH_2 - CH_2$$

$$O \qquad OH \qquad OR \qquad OR \qquad OR$$

$$OR \qquad OR \qquad OR$$
1. 2-dialkov vetbane

(h) Reaction with diazomethane:

$$R-OH+CH_2N_2 \rightarrow R-O-CH_3+N_2$$
(Ether)

(ii) **Alkylation**: $ROH + R_2'SO_4 \rightarrow ROR' + R'HSO_4$

(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 .

$$R - OH_2^+ + X^- \to {}^{\delta^-}X - -- R - -- OH_2^{\delta^+} \to R - X + H_2O$$
Protonated

1º alcohol

In secondary and tertiary alcohols, the $S_{\,_{N^1}}$ mechanism operates

$$R-OH \stackrel{\underline{H^+}}{\longleftarrow} R-OH_{2}^{+} \stackrel{-H_2O}{\longrightarrow} R^+ \stackrel{X^-}{\longrightarrow} R-X$$

(b) Reaction with PCl₅:

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

(c) Reaction with PCl₃:

(d) Reaction with thionyl chloride [SOCl₂]:

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

(e) Reaction with ammonia:

$$\begin{array}{c} ROH + NH_3 \xrightarrow{Al_2O_3} RNH_2 \\ \hline ROH + NH_3 \xrightarrow{Al_2O_3} ROH_2 \\ \hline ROH - ROH -$$

(f) Reaction with HNO_3 :

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

(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.

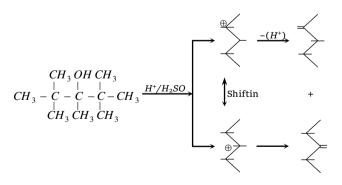
$$CH_3 - CH_2 - OH \xrightarrow{H_2SO_4} \xrightarrow{17} CH_2 = CH_2$$

$$CH_3 - CH_2 - OH \xrightarrow{H_2SO_4} \xrightarrow{110} C_2H_5HSO_4$$

$$CH_3 - CH_2 - OH \xrightarrow{H_2SO_4} \xrightarrow{Ethyl \ hydrogen}$$

$$C_2H_5O - C_2H_5$$

$$C_2H_5O - C_2H_5$$
Diethyl ether



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

$$CH_{2} = CH - CH - CH_{3} > CH_{3} - CH_{2} - CH - CH_{3}$$

$$OH \qquad OH$$

$$CH_{3} \qquad CH_{3} \qquad CH_{3}$$

$$CH_{3} - C - CH - CH_{3} \xrightarrow{H_{2}SO_{4} - H_{2}O} CH_{3} - C - CH - CH_{3} \rightarrow CH_{3}$$

$$CH_{3} CH_{3} OH \qquad CH_{3}$$

$$CH_{3} CH_{3} - C - CH - CH_{3} \xrightarrow{-H^{+}} CH_{3} - C = C$$

$$CH_{3} CH_{3} - C - CH - CH_{3} \xrightarrow{CH_{3} - H^{+}} CH_{3} - C = C$$

$$CH_{3} CH_{3} - C - CH - CH_{3} \xrightarrow{CH_{3} - H^{+}} CH_{3} - C = C$$

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

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

$$CH_{3} - C - CH_{3} - C - CH_{3}$$

$$CH_{3} - C - CH_{3} - C - CH_{3}$$

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$$CH_{3} - C - CH_{3} - C - CH_{3}$$

$$CH_{3} - C - CH_{3} - C - CH_{3}$$

(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.

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

$$H \qquad OH$$

$$Aldehy de \qquad Carboxy lic acid$$

$$2^{\circ} \rightarrow R - CH - R' \xrightarrow{CrO_{3}} R - C - R'$$

$$OH \qquad O$$
Secondary alcohol
$$CH_{3} \qquad CH_{3} \qquad CH_{3}$$

$$CH_{3} \qquad CH_{3} \rightarrow C - OH \xrightarrow{(Under strong condition)} CH_{3} - C = O$$

$$CH_{3} \qquad CH_{3} \rightarrow C + OH \xrightarrow{(Under strong condition)} CH_{3} - C = O$$

$$CH_{3} \qquad CH_{3} \rightarrow C + OH \xrightarrow{(Under strong condition)} CH_{3} - C = O$$

$$CH_{3} \qquad CH_{3} \rightarrow C + OH \xrightarrow{(Under strong condition)} CH_{3} - C = O$$

$$CH_{3} \rightarrow CH_{3} - C - OH \xrightarrow{(Under strong condition)} CH_{3} - C = O$$

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$$CH_{3} \rightarrow CH_{3} - C - OH \xrightarrow{(Under strong condition)} CH_{3} - C - OH$$

$$CH_{3} \rightarrow CH_{3}$$

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

(c) Catalytic oxidation/dehydrogenation

$$3^{\circ} \ CH_{3} - C - OH \xrightarrow{Cu,573 \, K} CH_{3} - C = CH_{2} + H_{2}O$$

$$CH_{3} \xrightarrow{CH_{3} - C - OH} \xrightarrow{Cu,573 \, K} CH_{3} - C = CH_{2} + H_{2}O$$

$$CH_{3} \xrightarrow{2-\text{Methy lpropene}} (Alkene)$$

$$(Tert. alcohol)$$

Important reagents used for oxidation of alcohols

- \bullet PCC [Pyridinium chloro chromate $(C_6H_5\ NH\ Cl\ CrO_3^-)$] 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.
- \bullet $H_2 CrO_4$ (chromic acid) to oxidise 1° alcohol to carboxylic acid.
- \bullet $\mathit{CrO}_3 \cdot H_2\mathit{SO}_4$ / 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.
- \bullet MnO_2 selectively oxidises the -OH group of allylic and benzylic 1° and 2° alcohols to give aldehyde and ketone respectively.
- \bullet 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.

(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.

Table: 26.1 Difference between methanol and ethanol

Methanol	Ethanol
(i) When <i>CH</i> ₃ <i>OH</i> is heated on	(i) It does not give
Cu coil it gives formalin like	formalin like smell.
smell.	
(ii) When <i>CH</i> ₃ <i>OH</i> 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

$$\begin{array}{c} C_{3}H_{7}OH \xrightarrow{SOCl_{2}} C_{3}H_{7}Cl \xrightarrow{\text{alc } KOH} CH_{3}CH = CH_{2} \\ \text{Propan-1-ol} \\ \text{(1° alc ohol)} \end{array}$$

(ii) Secondary alcohol into tertiary alcohol

$$\begin{array}{c|c}OH&O\\CH_3-CH-CH_3&\xrightarrow{[O]}K_2Cr_2O_7/H^+\\CH_3-CC-CH_3\\\text{(Iso-propyl alcohol)}\end{array}$$

$$CH_{3}^{MgBr} \rightarrow CH_{3} - \begin{matrix} OMgBr & OH \\ -C - CH_{3} & & -H^{+}, H_{2}O \\ -C - CH_{3} & & -H^{+}, H_{2}O \end{matrix} \rightarrow CH_{3} - \begin{matrix} -C - CH_{3} \\ -C - CH_{3} \\ -C - CH_{3} \end{matrix}$$

$$CH_{3}$$
2-Methylpropan-2-ol (2007) strain shall (2007)

(iii) Primary alcohol into tertiary alcohol

$$\begin{array}{c|c} CH_3 & CH_3 \\ CH_3 CH CH_2 OH & \xrightarrow{H_2SO_4, \text{ Heat}} & CH_3 \\ \text{2-Methyl propan-1-ol (1°)} & \text{Dehy dration} & CH_3 - C = CH_2 \xrightarrow{\textit{HBr}} & \text{Markowniko ffs} \\ \text{(Iso butyl alcohol)} & \text{Iso butyl alcohol)} & \text{Iso butyl alcohol} & \text{Iso butyl$$

$$\begin{array}{c} CH_3 & CH_3 \\ CH_3 - \overset{\mid}{C} - CH_3 & \xrightarrow{\text{aq. } KOH} & CH_3 - \overset{\mid}{C} - CH_3 \\ Br & OH \\ & & &$$

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

$$\begin{array}{c} CH_3OH & \xrightarrow{HI} CH_3I \xrightarrow{KCN} CH_3CN \\ & \xrightarrow{\text{Methanol}} \\ (1 \text{ carbon atom}) & \xrightarrow{4(H)} CH_3CH_2NH_2 \xrightarrow{HONO} CH_3CH_2OH \\ & \xrightarrow{\text{Ethanol}} \\ (2 \text{ carbon atoms}) & \\ \end{array}$$

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

$$\begin{array}{c} C_2H_5OH \xrightarrow{K_2Cr_2O_7,H^+} CH_3COOH \xrightarrow{NaOH} CH_3COONa \\ \xrightarrow{\text{Ethanol}} (2 \text{ carbon atoms}) \end{array}$$

$$\begin{array}{c} C_2H_5OH \xrightarrow{ROOH+CaO} CH_4 \xrightarrow{Cl_2} CH_3Cl \xrightarrow{\text{aq. KOH}} CH_3OH \\ \xrightarrow{\text{Methanol}} (\text{one carbon atom}) \end{array}$$

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	$R_2CH - OH \xrightarrow{\text{conc. } HCl / ZnCl_2 \text{ anhy.}} R_2 - CH - Cl \rightarrow \text{ ppt. appears with in 5 minutes}$
Tertiary	$R_3C - OH \xrightarrow{Z_3Cl_2/HCl} R_3C - Cl \rightarrow \text{ppt. appears immediately}$

(ii) *Victor mayer test*: Also known as RBW test. RBW → Red, Blue, White test.

Primary	$C_2H_5OH \xrightarrow{P+I_2} C_2H_5I \xrightarrow{AgNO_2} C_2H_5NO_2 \xrightarrow{HONO} CH_3 - C - NO_2 \xrightarrow{NaOH} CH_3 - C - NO_2$
	NOH NONa
	Nitrolic acid Sod. salt of nitrolic acid (Red colour)
Secondary	$(CH_3)_2 CHOH \xrightarrow{P+I_2} (CH_3)_2 CHI \xrightarrow{AgNO_2} (CH_3)_2 - CNO_2 \xrightarrow{HONO} (CH_3)_2 - CNO_2 \xrightarrow{NaOH} $ No reaction (Blue NO
	colour)
Tertiary	$(CH_3)_3COH \xrightarrow{P+I_2} (CH_3)_3Cl \xrightarrow{AgNO_2} (CH_3)_3CNO_2 \xrightarrow{HONO}$ No reaction (colourless)

Dihydric alcohols

These are compound containing two hydroxyl groups. These are dihydroxy derivatives of alkanes. Their general formula is $C_nH_{2n+2}O_2$. 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 O₂ in presence of Ag:

$$\begin{array}{c} CH_2 \\ || \\ CH_2 \\ CH_2 \end{array} + \frac{1}{2} O_2 \xrightarrow[Ag,200-400\,^{\circ}C]{} CH_2 \\ || \\ Ethy \text{ lene} \\ \end{array} \begin{array}{c} CH_2 \\ || \\ CH_2 \\ ||$$

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

$$\begin{array}{c} CH_2 \\ \parallel \\ CH_2 + HOCl \rightarrow \\ \parallel \\ CH_2Cl \\ \text{Ethy lene chlorohy drin} \end{array}$$

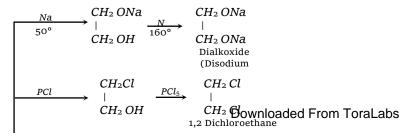
$$\begin{array}{c} CH_2OH \\ \longrightarrow \\ NaHCO_3 \longrightarrow \\ -NaHCO_3 \longrightarrow \\ -NaCl + CO_2 \end{array}$$

(ii) From 1, 2 dibromo ethane [Lab method]:

(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.

$$\begin{array}{c|c} R \\ \hline R \\ \hline \end{array} C = O + \begin{array}{c|c} C H_2OH \\ \hline CH_2OH \\ \hline \end{array} \rightarrow \begin{array}{c|c} R \\ \hline C \\ \hline \\ O - CH_2 \\ \hline \\ O - CH_2 \\ \hline \end{array}$$

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

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

(ii) By fermentation of sugar

$$C_{6}H_{12}O_{6} \xrightarrow{\text{Yeast} \atop \text{Na}_{2}SO_{3}} C_{3}H_{8}O_{3} + CH_{3}CHO + CO_{2}$$
Glycerol Acetaldehyde

(iii) From propene [Modern method]

$$\begin{array}{c|cccc} CH_3 & CH_2Cl & CH_2OH \\ \hline CH & CH_2 & CH_2 & CH \\ \hline CH_2 & CH_2 & CH_2 & CH_2 \\ \hline propene & Ally khloride & Ally kalcohol \\ \end{array}$$

$$\begin{array}{c} CH_2OH & CH_2-OH \\ \xrightarrow{HOCl} & CH & Cl & \xrightarrow{\text{aq. NaOH}} & CH-OH \\ CH_2-OH & CH_2-OH \\ \beta\text{-monochloro by drin} & \text{Glycerol} \end{array}$$

(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

(ii) Reaction with PCl₅, PBr₃ and PI₃

(iii) Reaction with HCl or HBr

$$\begin{array}{c|c} & CH_2Cl & CH_2Cl \\ \hline \xrightarrow{\text{Excess of } HCl} & CH Cl & + CH OH \\ \hline & & CH Cl & + CH OH \\ \hline & & CH_2OH & CH_2Cl \\ \hline & & & Glycerol \\ \alpha,\beta-\text{dichlorohy drin} & \alpha,\alpha'-\text{dichlorohy drin} \\ \hline & & (36\%) & (44\%) \end{array}$$

(iv) Reaction with HI

$$(a) \begin{tabular}{c|c} CH_2OH & CH_2I & CH_2 \\ $(a) \begin{tabular}{c|c} $CHOH+3HI$ & $Warm$ & CHI & \to & CH & $+$ & I_2 \\ CH_2OH & CH_2I & CH_2I & CH_2I \\ $I_{1,2,3}$-Tri-iodopropan e & $Ally liodide$ \\ CH_2 & CH_3 & CH_3 & CH_3 \\ $O(CH_2)$ & CH_3 & CH_3 & CH_3 & CH_3 \\ $O(CH_2)$ & CH_3 & $C$$

(v) Reaction with oxalic acid

(a) At 110°C Glycerol is formed

$$\begin{array}{c} CH_2OH \\ CH\ OH\ + HOOC - COOH \\ CH_2OH \end{array} \xrightarrow[Oxalic\ acid]{} CH_2OOC\ COOH \\ -H_2O \\ CH_2OH \end{array} \xrightarrow[Oxalic\ acid]{} CH_2OH \\ CH$$

$$\begin{array}{c} O \\ CH_2O-C-H \\ \longrightarrow CH_2OH \\ -CO_2 \\ \longrightarrow CH-OH \\ CH_2-OH \\ Glycerolmono formate \\ \end{array} \begin{array}{c} CH_2OH \\ \longrightarrow CHOH \\ -CH_2OH \\ Glycerol \\ Glycerol \\ \end{array}$$

(b) At 260°C, allyl alcohol is formed
$$CH_2OH$$
 CH_2OOC $CHOH + HOOC$ CH_2OH CH_2OH CH_2OH CH_2OH

$$\xrightarrow{-2CO_2} \xrightarrow{||} CH_2 \atop CH - CH_2OH$$
 Ally lalcohol

(vi) Dehydration

$$\begin{array}{c|c} CH_2OH & CH_2\\ | CHOH & \xrightarrow{\text{conc. } H_2SO_4 \mid P_2O_5 \mid KHSO_4} & CH\\ | CH_2OH & \xrightarrow{\Delta} & CH & + 2H_2O\\ | CHO\\ | CH$$

(vii) Oxidation

(viii) Reaction with nitric acid

$$\begin{array}{c} CH_2OH \\ | CHOH + 3HNO_3 & \xrightarrow{\text{conc.} H_2SO_4} & CH_2ONO_2 \\ | CH_2OH & CH_2ONO_2 & CH_2ONO_2 \\ | CH_2ONO_2 & \text{Gly cery limit rate (T.N.G.)} \end{array}$$

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.

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Oxalic acid

Unsaturated alcohols (Allyl alcohol)

(1) Preparation

(i) From allyl halide

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

(ii) By heating glycerol with oxalic acid:

$$\begin{array}{c|c} CH_2OH & CH_2OOC & CH_2 \\ |CHOH| + HOOC & |CH_2OH| & |CHOOC| & |CHOOC| \\ |CH_2OH| & CH_2OH & |CH_2OH| & |CH_2OH| \\ \end{array}$$

(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 CH₃CH₂CH₂OH Pt 1-propanol Br_{2} CH₂Br - CHBrCH₂OH 2, 3-dibromopropanol-1 HBrCH2BrCH2 CH2OH 3-Bromopropanol-1 CH2OHCHClCH2OH Glycerol β-monochlorohydrin →CH₂OH - CHOH - CH₂OH (0 +Glycerol $Na \longrightarrow CH_2 = CH - CH_2ONa$ $CH_2 = CH - CH_2OH$ (Allyl alcohol) $CH_3COOH \rightarrow CH_2 = CH - CH_2OOCCH_3$ Allyl acetate \rightarrow CH₂ = CH - CH₂Cl Allyl chloride COOH Oxidati HCOOHCOOHFormic acid Oxalic CH_2 - CH - CH_2 Br_2 BrBrOHHNO [O] CH₂ - CH - COOH 1 - 1 Br $(CH_3OH$ Zn $CH_2 = CH - COOH$ Acrylic acid

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

(i) From benzene sulphonic acid

$$\begin{array}{c} C_6H_6 \xrightarrow{H_2SO_4(\mathrm{fuming})} C_6H_5SO_3H \xrightarrow{NaOH} \\ \text{Benzene} \end{array}$$
 Benzene sulphonic acid

$$\begin{array}{c|c} C_6H_5SO_3Na & \xrightarrow{NaOH} & C_6H_5ONa & \xrightarrow{H^+/H_2O} & C_6H_5OH \\ \text{Sodium benzene sulphonate} & \xrightarrow{\text{Fuse}} & \text{Sodium phenoxide} & \xrightarrow{\text{or } CO_2/H_2O} & C_6H_5OH \\ \end{array}$$

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

$$SO_3H$$
 OK OH
 CH_3 CH_3 CH_3
 p -Toluene sulphonic P -

(ii) From benzene diazonium chloride

$$C_{6}H_{6} \xrightarrow{HNO_{3}} C_{6}H_{5}NO_{2} \xrightarrow{Sn/HCl} C_{6}H_{5}NH_{2}$$
Benzene $\xrightarrow{NaNO_{2}} C_{6}H_{5}N_{2}Cl$
Aniline
$$NH_{2} \xrightarrow{HNO_{4}} C_{6}H_{5}N_{2}Cl \xrightarrow{H_{2}O} C_{6}H_{5}OH$$
Phenol
$$NH_{2} \xrightarrow{NaNO_{2}} C_{6}H_{5}N_{2}Cl \xrightarrow{H_{2}O} C_{6}H_{5}OH$$
Phenol
$$NH_{2} \xrightarrow{HNO_{4}} CH_{3} \xrightarrow{M-Toluene} CH_{3}$$

$$m-Toluene \xrightarrow{diazonium} CH_{3}$$

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

(iii) From Grignard reagent

$$\begin{array}{c} C_6H_5Br + Mg \xrightarrow{\text{Either}} & C_6H_5MgBr \\ \text{Bromobenze ne} & & \\ \hline \\ & -\frac{o_2}{} \rightarrow C_6H_5OMgBr \xrightarrow{H_2O} & C_6H_5OH \\ & & \\ \hline \\ & & \\ \end{array}$$

(iv) From salicylic acid:

OH OH COOH
$$+ 2NaOH \xrightarrow{CaO} + Na_2CO_3 + H_2O$$
 Salicylic Phenol

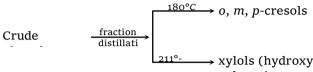
- (v) *Middle oil of coal tar distillation*: Middle oil of coal-tar distillation has naphthalene and phenolic compounds. Phenolic compounds are isolated in following steps.
- **Step I:** Middle oil is washed with H_2SO_4 . It dissolves basic impurities like pyridine (base).
- $\it Step~II: Ecessive cooling separates naphthalene (a low melting solid)$

 $Step\ III:$ 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.



(vi) Raschig's process

$$\begin{array}{c} C_6H_6 + HCl + \frac{1}{2}\,O_2 \xrightarrow{\quad CuCl_2/FeCl_3 \quad} C_6H_5Cl + H_2O \\ \text{Benzene} \end{array}$$

$$\begin{array}{ccc} C_6H_5Cl & +H_2O & \xrightarrow{425\,^o\,C} & C_6H_5OH & +HCl \\ \text{Chlorobenz ene} & \text{steam} & & \text{Phenol} \end{array}$$

(vii) Dow process

$$C_6H_5Cl + 2NaOH \xrightarrow{300^{o}C} C_6H_5ONa + NaCl + H_2O$$
Chlorobenz ene

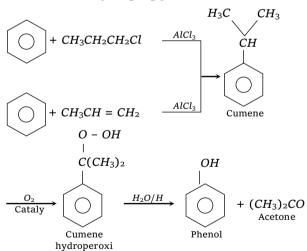
sodium phenoxide on treatment with mineral acid yields phenol.

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

(viii) Oxidation of benzene

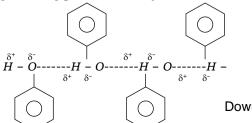
$$2C_6H_6 + O_2 \xrightarrow{V_2O_5} 2C_6H_5OH$$

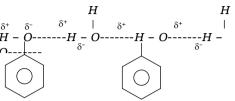
(ix) Oxidation of isopropyl benzene [Cumene]



(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.

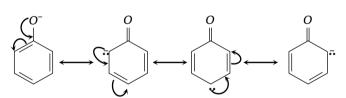
- (iii) It has a peculiar characteristic smell and a strong corrosive action on skin.
- (iv) It is sparingly soluble in water but readily soluble in organic solvents such as alcohol, benzene and ether.
- (v) It is poisonous in nature but acts as antiseptic and disinfectant.

(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.

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

Effects of substituents on the acidity of phenols

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

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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 :

 $p ext{-Nitrophenol} > o ext{-Nitrophenol} > m ext{-}$ 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 > p-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. $C_6H_5OH+NaOH\to C_6H_5ONa+H_2O$

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).

$$6 + FeCl_3 \rightarrow 3H^+ + \left[FeO - \right]_6^{3-} + 3HCl$$

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.

$$\begin{array}{c} C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O \\ \text{Sod. phenoxide} \\ C_6H_5ONa + ClCH_3 \rightarrow C_6H_5OCH_3 + NaCl \\ \text{Methyl phenylether (Anisole)} \\ \\ C_6H_5OK + IC_2H_5 \rightarrow C_6H_5 - O - C_2H_5 + KI \\ \text{Ethoxy benzene (Phenetol)} \\ \\ C_6H_5ONa + Cl - HC(CH_3)_2 \rightarrow C_6H_5 - O - HC(CH_3)_2 \\ \text{Isopropyl chloride} & \text{Isopropyl phenyl ether} \end{array}$$

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

$$C_6H_5OH + HOCH_3 \xrightarrow{\Delta, ThO_2} C_6H_5 - O - CH_3$$
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.

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

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

$$C_{6}H_{5}OH + Cl C - C_{6}H_{5} \xrightarrow{NaOH}$$
Benzoyl chloride
$$C_{6}H_{5} - O - C - C_{6}H_{5} + NaCl + H_{2}O$$
Phanul benzoyle

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.

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

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

(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.**

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

(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) $\it Reactions of benzene nucleus: The -OH group is ortho and para directing. It activates the benzene nucleus.$
- (a) ${\it Halogenation}$: Phenol reacts with bromine in carbon disulphide (or ${\it CHCl}_3$) at low temperature to form mixture of ${\it ortho}$ and ${\it para}$ bromophenol.

$$OH \qquad OH \qquad OH$$

$$+ Br_2 \qquad CCS_2 \qquad + \qquad Br$$

$$OH \qquad OH \qquad P^-$$

$$Br \qquad P^-$$

$$Br \qquad Br \qquad + 3HBr$$

$$2, 4, 6^-$$

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°C), the *ortho*-isomer is the major product, whereas at 100°C, it gives mainly the *para*-isomer.

(c) Nitration: Phenol reacts with dilute nitric acid at $5\text{-}10^{\circ}C$ 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.

$$OH \qquad OH \qquad OH \qquad OH \qquad \\ \hline \longrightarrow \qquad \\ \hline \stackrel{HNO_3(\text{dil.})}{(5^-)} \qquad OH \qquad \\ \hline \longrightarrow \qquad \\ NO_2 \qquad \\ NO_2 \qquad \\ NO_2 \qquad \\ P^- \qquad \\ \hline \\ NO_2 \qquad \\ P^- \qquad \\ \\ NO_3 \qquad \\ OH \qquad \\$$

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°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.

$$OH \qquad OH \qquad OH \qquad NO_2$$

$$\xrightarrow{HNO_3} \qquad H_2SO_4. \qquad NO_2$$

To get better yield of f icric acid, first sulphonation of phenol is made and then nitrated. Presence of $-SO_3H$ 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 QH ount of o-cresol is also QH

$$+ CH_3Cl \xrightarrow{AlCl} + CH_3$$

$$CH_3$$

$$CH_3$$

$$p\text{-Cresol}$$

$$(minor)$$

 $\it RX$ and $\it AlCl_3$ give poor yields because $\it AlCl_3$ 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:

$$C_{6}H_{5}OH + \begin{cases} CH_{3}CH = CH_{2} & OH \\ (CH_{3})_{2}CH - OH & OH \\ OH & OH \\ Acetyl chloride \end{cases} OH OH COCH_{3}$$

$$CH(CH_{3})_{2}CH - OH OH COCH_{3}$$

$$COCH_{3} & OH COCH_{3}$$

(e) Kolbe-Schmidt reaction (Carbonation):

ONa
OCOONa
OH
COONa
$$+ CO_2 \xrightarrow{130-} 6$$
Sodium
$$+ COOC_6H_5$$
OH
$$+ COOC_6H_5$$
Salol
$$+ COOCH_3$$
OCOOCH
Salicylic acid
OH
COOCH
$$+ COOCH_3$$
OCOOCH
OCOCH_3
OH
OCOCCH_3
OH
OCOCC

(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.

$$\begin{array}{c|c}
OH & & ONa \\
\hline
CHO & \\
Salicylaldehy & \\
OH & \\
\hline
CHCl_3 & \\
\hline
OH & \\
OH & \\
\hline
OH$$

(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).

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

(h) Mercuration

(i) Hydrogenation

$$OH \qquad OH$$

$$\downarrow \qquad \qquad \downarrow \qquad \qquad \downarrow$$

$$+ 3H_2 \qquad \stackrel{Ni}{\longrightarrow} \qquad Cyclohexanol$$

$$(C_6H_5OH \qquad (C_6H_{11},OH)$$

(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).

$$N = NCl + OH \xrightarrow{NaO - HCl}$$
 Benzene diazonium Phenol
$$N = N - OH \xrightarrow{NaO - HCl}$$
 Downloaded From ToraLabs
$$OH = N - OH$$

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).

OH

OH

Phenolphthale

$$OH \qquad OH \qquad OH \qquad OH \qquad \\ CH_2OH \qquad + CH_2OH \qquad + CH_2OH \qquad \\ benzyl \ alcohol \qquad CH_2OH \qquad \\ p-hydroxy \qquad \\ benzyl \ alcohol \qquad \\ D = 1 + CH_2OH \qquad \\ D = 1$$

Condensation
$$CH_2$$
 CH_2 CH_2 CH_2 CH_2 CH_2 CH_2

Polymer Bakelite (a

(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.

$$C_6H_5OH$$
 $OH \xrightarrow{O_2 \text{ by or}} O \xrightarrow{P_2 \text{ or}} O \xrightarrow{C_6H_5OH} O \xrightarrow{P_2 \text{ or}} O \xrightarrow{C_6H_5OH} O \xrightarrow{P_2 \text{ or}} O \xrightarrow{C_6H_5OH} O \xrightarrow{P_2 \text{ or}} O$

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

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

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- (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.
- $\mbox{\ensuremath{(x)}}$ In the preparation of disinfectants, fungicides and bactericides.

- (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
$$\xrightarrow[\text{Excess of water}]{NaNO_2}$$
 Red colour $\xrightarrow[\text{Excess}]{NaOH}$ 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.

(5) Tests of phenol

Table: 26.2 Difference between phenol and alcohol

Table : 26.2 Difference between phenol and alcohol					
Property	Phenol (C_6H_5OH)	Alcohol (C₂H₅OH)			
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 FeCl 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 HCHO	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 PCl ₅	Mainly forms triphenyl phosphate.	Forms ethyl chloride			
Iodoform test	Does not show.	Positive.			

Derivatives of phenol

NITROPHENOLS

(1) Preparation

(iii)
$$C_6H_4$$
 NO_2 OH_4 NO_2 $O-$ and $p-$ chloro nitrobenze ne OH_4 NO_2 $O-$ and $p-$ nitropheno 1 OH_4 OH

(iv)
$$NO_2$$
 NH_2 NH_4HS or NO_2 NO_2 NO_2 NO_2 NO_2 NO_2 NO_2

$$N_2Cl$$
 OH
 N_2Cl OH

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

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

$$C_6H_4$$
 OH
 OH
 Br
 Br
 Br
 Br
 Br
 Br

2,4,6 Tribromophenol

Picric acid (2, 4, 6-trinitrophenol)

(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

$$OH$$
 NO_2
 O_2N
 NO_2
 O_2N
 NO_2
 NO_2
 NO_2

Picric acid (2, 4, Downloaded From ToraLabs

(ii) From phenol through disulphonic acid

(iii)
$$OH$$

$$O_2N$$

$$+ [O] \xrightarrow{Ke_3Fe(CN)} O_2N$$

$$NO_2$$

$$NO_2$$

$$TNB$$

$$NO_2$$

$$Picric$$

(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 with NH_3 yields picramide. NH_2

$$O_2N$$
 NO_2
 O_2N
 NO_2
 O_2N
 NO_3
 NO_4
 NO_2
 NO_4
 NO_2
 NO_4
 NO_2
 NO_4
 NO_2
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 NO_9

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)

(1) Preparation

(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.

$$\begin{array}{c|c}
O & OH & O \\
OH & OH \\
C & OH$$

(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).

$$SO_3H$$
 ONA OH

 SO_3H ONA

 ONA OH

 ONA OH

 ONA OH

(2) **Properties:** It is a colourless crystalline solid, melting points $110^{\circ}C$. 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.

$$OH \qquad OH \\ Br \qquad Br \\ OH \qquad OH \\ OH \qquad OH$$

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

$$OH$$
 O_2N
 O_2N
 OH
 OH
 OOH
 OOH

It condenses with phthalic anhydride and forms luorescein. OH

fluorescein. OH

$$O = C$$
 $O = C$
 O

With nitrous acid, it forms 2, 4 dinitrosoresorcinol

$$OH \qquad OH \qquad O$$

$$NO \qquad NOH$$

$$OH \qquad OH \qquad NOH$$

$$OH \qquad NOH$$

$$OH \qquad NOH$$

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

(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 $(H_2SO_3/-V+SO_2)$.

$$H_2SO_3$$
 $O + SO_2$).
 $O + SO_2 + 2H_2O \rightarrow HO$ $OH + H_2SO_4$
 $OH + H_2SO_3 + H_2O$ $OH + H_2SO_4$

(p-Benzoquinone is obtained by oxidation of aniline)

$$\begin{array}{c|c} NH_2 & O & OH \\ \hline \\ \hline \\ MnO_2/H_2SO \end{array} \begin{array}{c} \hline \\ \hline \\ O & OH \\ \hline \\ O & OH \\ \hline \\ Quino \end{array}$$

(2) **Properties:** It is a colourless crystalline solid, melting points 170°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 $220^{\circ}C$.

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

$$CH_3$$
 O_2N
 NO_2
 NO_2

COOH

$$H_2N$$
 NH_2
 H_2O/H^+
 $100^\circ C$
 OH
 $+CO_2+3NH_4Cl$

Phlorogluci

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

$$OH \qquad OH \qquad OH$$

$$OH \qquad OH$$

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

Sodium ethoxide Ethyl bromide

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 methyl ether
$$C_2H_5ONa + C_2H_5Br \rightarrow C_2H_5OC_2H_5 + NaBr$$

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

Ethoxy etha ne

- (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.

$$CH_3 \qquad CH_3 \\ C_2H_5Br + NaO - C - CH_3 \rightarrow C_2H_5 - O - C - CH_3 \\ Ethyl \ bromide \\ CH_3 \qquad CH_3 \\ Sodium \ salt \ of tert, \ but \ V \ l \ alcohol$$
 Ethyl tert, but \ l \ ether \ but \ l \ ether \ but \ V \ l \ alcohol

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

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

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

$$CH_3 \xrightarrow{C} CH_3 \xrightarrow{C} CH_3$$

$$CH_3 - C \oplus + C_2H_5O^- \rightarrow CH_3 - C \oplus C_2H_5OH$$

$$CH_2 - H \xrightarrow{C} CH_2$$

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

(ii) By heating alkyl halide with dry silver oxide

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

$$2C_2H_5Br+Ag_2O \xrightarrow{\text{heat}} C_2H_5OC_2H_5+2AgBr \text{ Ethyl bromide}$$
 Diethyl ether

- (2) From alcohols
- (i) By dehydration of alcohols
- (a) With conc. H₂SO₄ at 140° C

$$ROH + HOR \xrightarrow{H_2SO_4(\text{conc.})} ROR + H_2O$$
.

 $140^{\circ}C$ Ether

- ☐ 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: $2ROH \xrightarrow{Al_2O_3} R - O - R + H_2O$

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

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

- (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

$$\begin{array}{c} > C = C < +R - OH + \begin{array}{c} Hg[OOCCF_3]_2 \\ \text{Mercuric rifluoro acetate} \end{array}$$

$$\rightarrow - \begin{array}{c} \begin{matrix} \\ \\ \\ \end{matrix} - \begin{array}{c} \\ \end{matrix} - \begin{array}{c} \\ \end{matrix} - \begin{array}{c} \\ \\ \end{matrix} - \begin{array}{c} \\ \end{matrix} - \begin{array}{c} \\ \\ \end{matrix} - \begin{array}{c} \\ \end{matrix} - \end{array} - \begin{array}{c} \\ \end{matrix} - \end{array} - \begin{array}{c} \\ \end{matrix} - \begin{array}{c} \\ \end{matrix} - \end{array} - \begin{array}{c} \\ \end{array} - \begin{array}{c} \\$$

- $\ \square$ This is the best method for the preparation of tethers.
- (4) Reaction of lower halogenated ether with grignard reagent

$$\begin{array}{ccc} ROCH_2X + XMgR' \rightarrow ROCH_2R' + MgX_2 \\ \text{Halogenate d} & \text{Grignard} & \text{Higher} \\ \text{ether} & \text{reagant} & \text{ether} \end{array}$$

- (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.
- \Box 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.

$$R > O \dots H \longrightarrow O$$
Ether
 $H \dots O < R$
Ether

- $\ \square$ 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.

$$H = \begin{matrix} R & R & R \\ | & | & | \\ O - - - H - O - - - H - O - - - \end{matrix} \\ \text{hy drogen bonding in alcohols} \begin{matrix} R & R \\ | & | \\ No \text{ hy drogen bond in ether} \end{matrix}$$

(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:

$$\begin{split} & CH_3CH_2OCH_2CH_3 \xrightarrow{Cl_2} CH_3CHClOCH_2CH_3 \\ & \text{Diethy lether} \end{split} \xrightarrow{Cl_2} CH_3CHClOCH_2CH_3 \\ & (\alpha\text{-Monochloro diethy lether}) \end{split}$$

$$& CH_3CH_2OCH_2CH_3 \xrightarrow{Cl_2} CH_3CHClOCHClCH_3 \\ & \text{Diethy lether} \end{split} \xrightarrow{(\alpha,\alpha'\text{-Dichlorodiethy lether})} CH_3CHClOCHClCH_3 \\ & (\alpha,\alpha'\text{-Dichlorodiethy lether}) \end{split}$$

$$& C_2H_5OC_2H_5 + 10Cl_2 \xrightarrow{(l_2)} C_2Cl_5OC_2Cl_5 + 10HCl$$

$$& (\text{Perchlorodiethy lether}) \end{split}$$

(ii) $\emph{Burning}$: Ethers are highly inflammable. They burn like alkanes.

$$C_2H_5 - O - C_2H_5 + 6O_2 \rightarrow 4CO_2 + 5H_2O_2$$

- (2) Reaction due to ethernal oxygen
- (i) Peroxide formation:

$$C_2H_5\stackrel{\cdots}{O}C_2H_5+\stackrel{\cdots}{O}:\to (C_2H_5)_2O\to O\;.$$

- (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.
- $\ \square$ 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 to 6)

(ii) Oxidation with K2Cr2O7 / H®

$$R - \stackrel{\alpha}{CH}_2 - O - \stackrel{\alpha'}{CH} \stackrel{R'}{<}_{R'}$$

- (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.

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

$$\xrightarrow{K_{2}Cr_{2}O_{7}} CH_{3} - COOH + CH_{3} - CH_{2} - COOH$$

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

$$CH_{3}$$

$$\xrightarrow{K_2Cr_2O_7} CH_3 - COOH + CH_3 - C - CH_3$$

(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.

$$C_2H_5OC_2H_5 + HCl \rightarrow (C_2H_5)_2 \stackrel{O}{O^+} Cl^-$$
 or

Diethyloxonium chloride

$$[(C_2H_2)_2O\cdot H]^+Cl^2$$

$$C_2H_5OC_2H_5 + H_2SO_4 \rightarrow (C_2H_5)_2 \stackrel{+}{O} + HSO_4^- \text{ or } H$$
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.

$$\begin{array}{c|c} (C_2H_5)_2 & O & Cl & \xrightarrow{H_2O} & (C_2H_5)_2O + HCl \\ & H & & \text{Diethy lether} \\ O & \text{Oxonium salt} \end{array}$$

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

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

- \Box 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**.

$$\begin{array}{c} CH_3CH_2 \nearrow O : +BF_3 \rightarrow \begin{array}{c} CH_3CH_2 \nearrow O \rightarrow BF_3 \\ CH_3CH_2 \nearrow O \rightarrow BF_3 \\ \end{array}$$
 Boron trifluoride etherate (complex)

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

$$2(CH_3CH_2)_2O + RMgX \rightarrow \underbrace{R}_{(CH_3CH_2)_2O} \underbrace{Mg}_{Grignard\ reagent\ etherate} X$$

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 : $ROR + H_2O \xrightarrow{H_2SO_4} 2ROH$

$$\begin{array}{c} C_2H_5OC_2H_5 + H_2O \xrightarrow{\quad H_2SO_4\quad} 2C_2H_5OH \\ \text{Diethylether} \end{array}$$
 Ethanol

(b) With conc. H_2SO_4 :

$$C_2H_5OC_2H_5 + H_2SO_4 \rightarrow C_2H_5OH + C_2H_5HSO_4 \\ C_2H_5OH + H_2SO_4 \rightarrow C_2H_5HSO_4 + H_2O$$

$$C_2H_5OC_2H_5 + 2H_2SO_4 \rightarrow 2C_2H_5HSO_4 + H_2O$$
Diethylether Ethyl hydrogen sulphate

(ii) Action of hydroiodic acid

(a) With cold HI

$$\begin{array}{ccc} C_2H_5OC_2H_5 + HI & \xrightarrow{\text{Cold}} & C_2H_5I + C_2H_5OH \\ \text{Diethy lether} & \text{Ethy liodide} & \text{Ethylacohol} \end{array}$$

$$OC_2H_5$$
 OH $+ C_2H_5Br$ Phenyl ethyl Phenol Ethyl bromide

(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.

(v) Reaction with acetyl chloride

(vi) Reaction with acid anhydride

$$CH_3CO \cdot O \cdot OCCH_3 + C_2H_5 \cdot O \cdot C_2H_5$$
Acetic anny dride Diethy lether

$$\xrightarrow{\text{ZnCl}_2} 2CH_3COOC_2H_5$$
Ethylacetate

(vii) **Dehydration**

$$C_2H_5OC_2H_5 \xrightarrow{Al_2O_3} 2CH_2 = CH_2 + H_2O$$

(viii) Reaction with carbon mono oxide

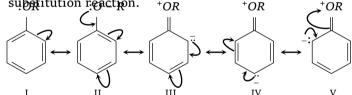
$$C_2H_5OC_2H_5 + CO \xrightarrow{BF_3/150\,{}^{o}C} C_2H_5COOC_2H_5$$
Diethylether $C_2H_5COOC_2H_5$
Ethyl propionate

(ix) Action of bases

$$\stackrel{+}{LiC}H_{3} + H - CH_{2} - CH_{2} - CH_{2} - CH_{3}$$

$$\rightarrow CH_{4} + CH_{2} = CH_{2} + \stackrel{+}{LiO}C_{2}H_{5}$$

(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.



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) broffde catalyst. QCH_3 QCH_3

Anisol

$$Br_2$$
 CS_2
 Br_2
 Br_2

Para isomer is obtained in 90% yield.

(ii) Friedel craft reaction

$$OCH_3$$
 OCH_3 $OCH_$

$$OCH_3 \qquad OCH_3 \qquad OCH_$$

 $\ \square$ Ethers are relatively less reactive than phenol towards electrophilic substitution reaction.



- \mathcal{E} Methyl alcohol (CH_3OH) is called wood spirit. It is obtained by destructive distillation of wood. Drinking of methanol causes blindness.
- \mathcal{E} 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.
- € 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%).
- \mathcal{L} Fusel oil is a mixture of n-propyl alcohol, n-butyl alcohol, n-amyl alcohol and isoamyl alcohol.
- $\boldsymbol{\mathscr{Z}}$ 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

 $CH_3OH > C_2H_5OH > (CH_3)_2CHOH > (CH_3)_3C - OH$ $HCOOH > CH_3COOH > (CH_3)_2CH - COOH > (CH_3)C -$ COOH.

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

$$CH_{3} - \begin{matrix} OH & OH \\ & & & \\ CH_{3} - \begin{matrix} C \\ C \\ & \\ \end{matrix} \\ CH_{3} \end{matrix} CH_{3} \xrightarrow{H^{+}} \begin{matrix} CH_{3} \\ & \\ & \\ \end{matrix} \\ CH_{3} \end{matrix} CH_{3} \xrightarrow{P_{\text{inacolone}}} CH_{3} \xrightarrow{P_{\text{inacolone}}} CH_{3}$$

- \varnothing In general, acid strength increases as Cresols << Phenol << p-chlorophenol << m-Nitrophenol << o-Nitrophenol << Picric acid.
- € 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.
- $\boldsymbol{\varkappa}$ 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.
- Æ 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.