hydric = (OH) group

Unit - Alcohol

→ General formula :- $C_nH_{2n+2}O$ i.e $C_nH_{2n+1}(OH)$

→ Representative formula R - OH

⇒ Hydrocarbon from which at least one hydrogen is replaced by hydroxy group is called alcohol.

Depending on no. of hydroxy group present, alcohols are monohydric, dihydric, trihydric and polyhydric alcohol.

* classification of monohydric alcohols :-

① primary alcohol (pri.) Eg. CH_3-CH_2-OH (1) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_2$ (CH_3 on CH)

② secondary alcohol (sec.) Eg :- $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$ (2) $CH_3-\underset{\underset{OH}{|}}{CH}-\underset{|}{CH}-CH_3$ (2, CH_3)

③ Tertiary alcohol (tert.) Eg :- $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$ (3)

* Nomenclature :-

→ common system :- alkyl alcohol (n, iso, neo- or sec, tert.)

→ IUPAC Name :- prefix + word root + pri. suff + ol

Eg's	Formula	common Name	IUPAC NAME
(1)	CH_3-OH	Methyl alcohol	Methanol
(2)	CH_3-CH_2-OH	Ethyl alcohol	Ethanol
(3)	$CH_3-CH_2-CH_2-OH$	n-propyl alcohol	propan-1-ol
(4)	$CH_3-\underset{OH}{CH}-CH_3$	sec-propyl alcohol (iso-propyl alcohol)	propan-2-ol
(5)	$CH_3-\underset{CH_3}{CH}-CH_2-OH$	iso-Butyl alcohol	2-methyl propan-1-ol
(6)	$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$	tert-Butyl alcohol	2-methyl propan-2-ol
(7)	$CH_3-CH_2-\underset{OH}{\overset{CH_3}{CH}}$	sec-Butyl alcohol	Butan-2-ol
(8)	$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-OH$	neo-pentyl alcohol	2,2-Dimethyl propan-1-ol
(9)	$\underset{OH}{CH_2}-\underset{OH}{CH_2}$	ethylene glycol	Ethane-1,2-diol
(10)	$\underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2}$	Glycerol	propane-1,2,3-triol.

Isomerism:-

Eg

① Chain Isomerism:-

Eg:-

$C_4H_{10}O$; $CH_3-CH_2-CH_2-CH_2-OH$ $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

② position Isomerism:-

Eg $C_4H_{10}O$ $CH_3-CH_2-CH_2-CH_2-OH$

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

(iii) Functional Isomerism:-

(a) Alcohol and ether are the functional isomer of each other.

Eg C_2H_6O

CH_3-CH_2-OH (alcohol)

CH_3-O-CH_3 (ether)

methanal is only one aldehyde which reacts with grignard reagent to form primary alcohol.

* General method of preparation of alcohol:

① From haloalkane :-

$$R-X + KOH_{(aqu.)} \xrightarrow{\Delta} R-OH + KX$$

$$CH_3-CH_2-Cl + KOH_{(aqu.)} \xrightarrow{\Delta} CH_3-CH_2-OH + KCl$$

② From aldehyde and Ketone

① By treatment with Grignard reagent:

$$R-mgx + \underset{\text{aldehyde (methanal)}}{H-\overset{O}{\overset{\|}{C}}-H} \longrightarrow R-\overset{O-mgx}{\overset{|}{C}}H_2 \xrightarrow[\Delta]{H_3O^+} R-\overset{OH}{\overset{|}{C}}H_2 + mg(OH)_x$$

1.

$$R'-mgx + \underset{\text{aldehyde}}{R-\overset{O}{\overset{\|}{C}}-C} \longrightarrow R-\overset{O-mgx}{\overset{|}{\underset{R'}{C}}}-H \xrightarrow{H_3O^+} R-\overset{OH}{\overset{|}{\underset{R'}{C}}}-H + mg(OH)_x$$

2.

$$R'-mgx + R-\overset{O}{\overset{\|}{C}}-R \longrightarrow R-\overset{O-mgx}{\overset{|}{\underset{R'}{C}}}-R \xrightarrow{H_3O^+} R-\overset{OH}{\overset{|}{\underset{R'}{C}}}-R + mg(OH)_x$$

3.

② By reduction :-

$$\underset{\text{aldehyde}}{R-\overset{O}{\overset{\|}{C}}-H} + H_2 \xrightarrow[\Delta]{Ni} R-\overset{OH}{\overset{|}{\underset{H}{C}}}-H \text{ or } R-CH_2-OH$$

$$R-\overset{O}{\overset{\|}{C}}-R \quad + [H] \xrightarrow{LiAlH_4} R-\overset{OH}{\overset{|}{C}}H-R$$

Ketone (2)

(3) from ester (by hydrolysis) :-

$$R-COOR' + H_2O \underset{\Delta}{\overset{H^+}{\rightleftharpoons}} R-OH + R-COOH$$

$$CH_3-COOC_2H_5 + H_2O \underset{\Delta}{\overset{H^+}{\rightleftharpoons}} C_2H_5OH + CH_3-COOH$$

Ethyl ethanoate

(4) From primary amine

$$R-NH_2 + HNO_2 \xrightarrow[0^\circ C \text{ to } 5^\circ C]{NaNO_2 + HCl} R-OH + N_2 + H_2O$$

When primary amine is treated with nitrous acid ~~in presence of~~ obtain from sodium nitrite and hydrochloric acid at 0°C to 5°C temperature, alcohol is formed.

$$R-NH_2 + HNO_2 \xrightarrow[0^\circ C \text{ to } 5^\circ C]{NaNO_2 + HCl} R-OH + N_2 + H_2O$$

$$CH_3-CH_2NH_2 + HNO_2 \xrightarrow[0^\circ C \text{ to } 5^\circ C]{NaNO_2 + HCl} CH_3-CH_2-OH + N_2 + H_2O$$

(5) From alkene (Industrial method)

(i) By addition of water

$$CH_3-CH=CH_2 + H_2O \xrightarrow[\Delta]{H^+} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_3 + H_2O \xrightarrow[\Delta]{H^+} CH_3-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$$

(ii) By oxo- process :-

When alkene is treated with mixture of carbon monoxide (CO) and Hydrogen gas in presence of dicobaltocta-carbonyl as catalyst at high temperature and high pressure, it under goes carbanylation reaction, producing aldehyde which on reduction gives alcohol. This method of preparation of alcohol is called oxo- process.

$$CH_2=CH_2 + CO + H_2O \xrightarrow[\text{High T., High p.}]{[Co_2(CO)_8]} CH_3-CH_2-CHO \xrightarrow[\Delta]{H_2\ Ni} CH_3-CH_2-CH_2-OH$$

Molecular molecular formula of ethene: ethanol

$2 \times BH_3$

B_2H_6 = Diborane.

(6) By hydroboration oxidation process

$$2R-CH=CH_2 + BH_3 \rightarrow (R-CH_2-CH_2)_3B$$

Trialkyl borane.

$$(R-CH_2-CH_2)_3B \xrightarrow{H_2O_2, OH^-} 3R-CH_2-CH_2-OH + B(OH)_3$$

OR,

$$3R-CH=CH_2 + BH_3 \rightarrow R-CH_2-CH_2-B(CH_2-CH_2-R)_2$$

$$R-CH_2-CH_2-B(CH_2-CH_2-R)_2 \xrightarrow{H_2O_2, OH^-} B(OH)_3 + R-CH_2-CH_2-OH$$

* Manufacture of ethyl alcohol by Fermentation process

⇒ The proces of degradation (braking) of complex organic molecule into simple molecule with the help of biological catalyst, enzyme is called fermentation.

There are two major source for manufacturing of ethyl alcohol by fermentation process. They are

(i) Molasses

(ii) Starch

glucose (aldehyde) functional group.

fructose (ketonic functional group.

* Manufacture of ethyl alcohol by fermentation of molasses:

The mother liquor left after fermentation of concentrated sugarcane juice is called molasses. It mainly contain sucrose.

Manufacturing of ethyl alcohol by fermentation of molasses (sucrose) involves following reaction.

(i) Sucrose is converted into glucose and fructose by invertase enzyme

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(ii) Glucose & fructose are converted into ethyl alcohol by zymase enzyme.

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

Thus obtained liquid contains about 8 to 15% alcohol which is called wash. It is subjected to fractional distillation which increases the concentration of alcohol up to 95%. This concentration of alcohol is called rectified Spirit (Industrial alcohol). It is subjected to distillation along with CaO followed by redistillation with

calculated amount of sodium, calcium to get 100% alcohol. It is called absolute alcohol.

To prevent misuse of alcohol, it is mixed with small amount of poisonous compound like methanol, $CuSO_4$, pyridine. It is called denaturation of alcohol.

Alcohol containing 4% methanol, very small amount of $CuSO_4$ and pyridine is called methylated alcohol or spirit.

* Manufacture of ethyl alcohol by fermentation of starch.

→ Wheat, maize, rice, potato etc. are major source of starch. Manufacturing of ethyl alcohol by fermentation of starch involves following reaction:

i) Starch is converted into maltose by diastase enzyme.

$$\underset{\text{(Starch)}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{diastase}} \underset{\text{(maltose)}}{nC_{12}H_{22}O_{11}}$$

ii) Maltose is converted into glucose by maltase enzyme

$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{maltase}} 2C_6H_{12}O_6$
(glucose)

iii.) Glucose is converted into ethanol by zymase enzyme

$C_6H_{12}O_6 \xrightarrow{\text{zymase}} 2CH_3-CH_2-OH + 2CO_2$

* physical properties of alcohol

① physical state:-

Lower member of alcohols upto twelve carbon atoms are colourless, volatile, liquid with characteristics alcoholic smell and burning state. Higher members are colourless, odourless, taskless, waxy acid.

② Boiling point:-

As size and molecular mass increase the boiling point also increases because.....

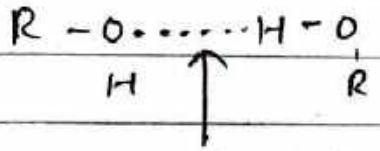
Eg CH_3-CH_2-OH < $CH_3-CH_2-CH_2-OH$

In case of isomeric alcohol as branching increases boiling point decreases because.....

Eg (a) $CH_3-CH_2-CH_2-CH_2-OH$ > $CH_3-\underset{CH_3}{\overset{CH_3}{|}}CH-CH_2-OH$ > $CH_3-\underset{CH_3}{\overset{CH_3}{|}}C-OH$

(b) 1° -alcohol > 2-alcohol > 3-alcohol

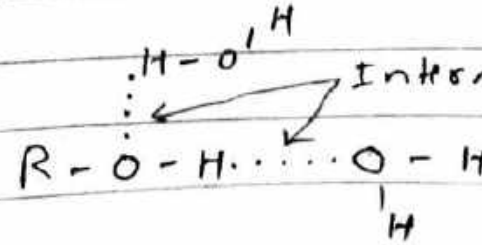
Alcohols have high boiling point than alkane, haloalkane, ether, aldehyde and ketone having comparable molecular mass because alcohol can form inter-molecular hydrogen bond but other cannot form intermolecular hydrogen bond.



③ Solubility :-

Alcohols are soluble in water because they can form intermolecular hydrogen bond with water.

But as molecular mass increases solubility decreases because hydro phobic interaction increases.



* Chemical properties of alcohol.

1. Reaction due to cleavage of R-$\overset{\zeta}{O}$H bond
2. Reaction with acid halide

$$R-OH + HX \longrightarrow R-X + H_2O$$

$$CH_3-CH_2-OH + HCl \xrightarrow{anhy.\ ZnCl_2} CH_3-CH_2-Cl + H_2O$$

(ii) Reaction with ammonia

$$R-OH + NH_3 \xrightarrow[-H_2O]{Al_2O_3,\ 350^\circ C} \underset{(1)}{R-NH_2} \xrightarrow[-H_2O]{ROH} \underset{(2)}{R-NH-R} \xrightarrow[-H_2O]{R-OH} \underset{(3)}{R_3N}$$

(2) Reaction due to ~~change~~ cleavage of R-O-$\overset{\zeta}{H}$ bond

(1) Reaction with active metal:-

When alcohol is treated with active metal like sodium(Na), K, Al, Ca, hydrogen gas is released. This reaction shows acidic nature of alcohol.

$$2R-OH + 2Na \longrightarrow \underset{\text{sodium alkoxide}}{2R-ONa} + H_2$$

$2CH_3-CH_2-OH + 2Na \rightarrow 2CH_3-CH_2ONa + H_2$
Sodium ethanoide

(ii) Esterification:-

When carbonylic acid is heated with alcohol in presence of concentrated conc.H_2SO_4, ester with fruity smell is formed.

This reaction is used as test reaction for carbonylic acid as well as alcohol

$R'-OH + R-COOH \underset{}{\overset{conc.H_2SO_4}{\rightleftharpoons}} R-COOR' + H_2O$

$CH_3-CH_2-OH + CH_3-COOH \overset{conc.H_2SO_4}{\rightleftharpoons} CH_3-COOC_2H_5 + H_2O$

(ii) Reaction with Grignard reagent.

$R'-OH + R'-MgX \rightarrow R-H + Mg(OR)X$

$CH_3-OH + CH_3-CH_2-MgBr \rightarrow CH_3-CH_3 + Mg(OCH_3)Br$

(3) Reaction due to participation of alkyl group and hydroxy group.

(i) oxidation:-

primary alcohol on oxidation with anhy. CrO_3 or pcc or $KMnO_4/H^+$ or $K_2Cr_2O_7/H^+$

etc aldehyde with same number of carbon atom whose further oxidation gives carbonylic acid.

$$R-\underset{1^\circ}{CH_2-OH} \xrightarrow[\Delta]{PCC} R-CHO \xrightarrow[\Delta]{PCC} R-COOH$$

$$CH_3-CH_2-OH \xrightarrow[\Delta]{PCC} CH_3-CHO \xrightarrow[\Delta]{PCC} CH_3-COOH$$

PCC = Pyridinium chlorochromate.

Secondry alcohol on oxidation with $KMnO_4/H^+$ or $K_2Cr_2O_7/H^+$ gives Ketone whose further oxidation takes place at high temperature and high pressure producing carbonylic acid by cleavage of Ketone.

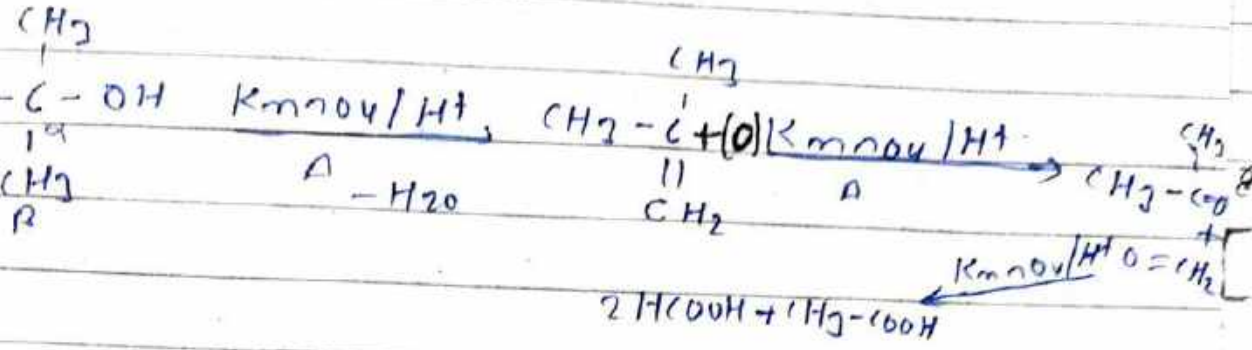
Cleavage of Ketone takes place in such a way that carbonyl carbon remains with that alkyl group which has less no. of carbon atom.

$$\underset{(2)}{CH_3-\overset{OH}{\overset{|}{CH}}-CH_3} \xrightarrow[\Delta]{KMnO_4/H^+} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{High T. / High P.}]{KMnO_4/H^+} HCOOH + CH_3-COOH$$

$$CH_3-CH_2-\overset{OH}{\overset{|}{CH}}-CH_3 \xrightarrow{[O]} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{[O]} 2\,CH_3-COOH$$

$$CH_3-CH_2-CH_2-\overset{OH}{\overset{|}{CH}}-CH_3 \xrightarrow{[O]} CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{KMnO_4/H^+} CH_3-CH_2-COOH + CH_3-COOH$$

* oxidation of tertiary alcohol.



ii Dehydration:-

1. Intermolecular dehydration:-

primary alcohol

On heating with conc. H_2SO_4 at 140°C or Al_2O_3 at 250°C under goes intermolecular dehydration producing ether

$$2\,CH_3-CH_2-OH \xrightarrow[140^\circ C]{conc.\ H_2SO_4} CH_3-CH_2-O-CH_2-CH_3 + H_2O.$$

2. ~~Intermolecular~~ .

2. Intramolecular dehydration:-

Alcohols on heating with conc. H_2SO_4 at 170°C or Al_2O_3 at 350°C under go intermolecular dehydration producing alkene.

$$CH_3-CH_2-OH \xrightarrow[170^\circ C]{conc.\ H_2SO_4} CH_2=CH_2 + H_2O$$

(iii) Dehydrogenation reaction :-

When alcohol is heated with red hot copper with 300°c. it under goes dehydrogenation reaction producing aldehyde or Ketone.

$$R-\underset{\alpha}{CH_2}-OH \xrightarrow[300^\circ c]{\text{red hot copper}} R-CHO + H_2$$

(aldehyde)

$$R-\underset{R}{\underset{|}{CH}}-OH \xrightarrow{\text{red hot copper}} R-\underset{R}{\underset{|}{C}}=O + H_2$$

(Ketone)

$$CH_3-\underset{CH_3}{\underset{|}{CH}}-OH \xrightarrow{\text{red hot copper}} CH_3-\underset{CH_2}{\underset{||}{C}} + H_2O$$

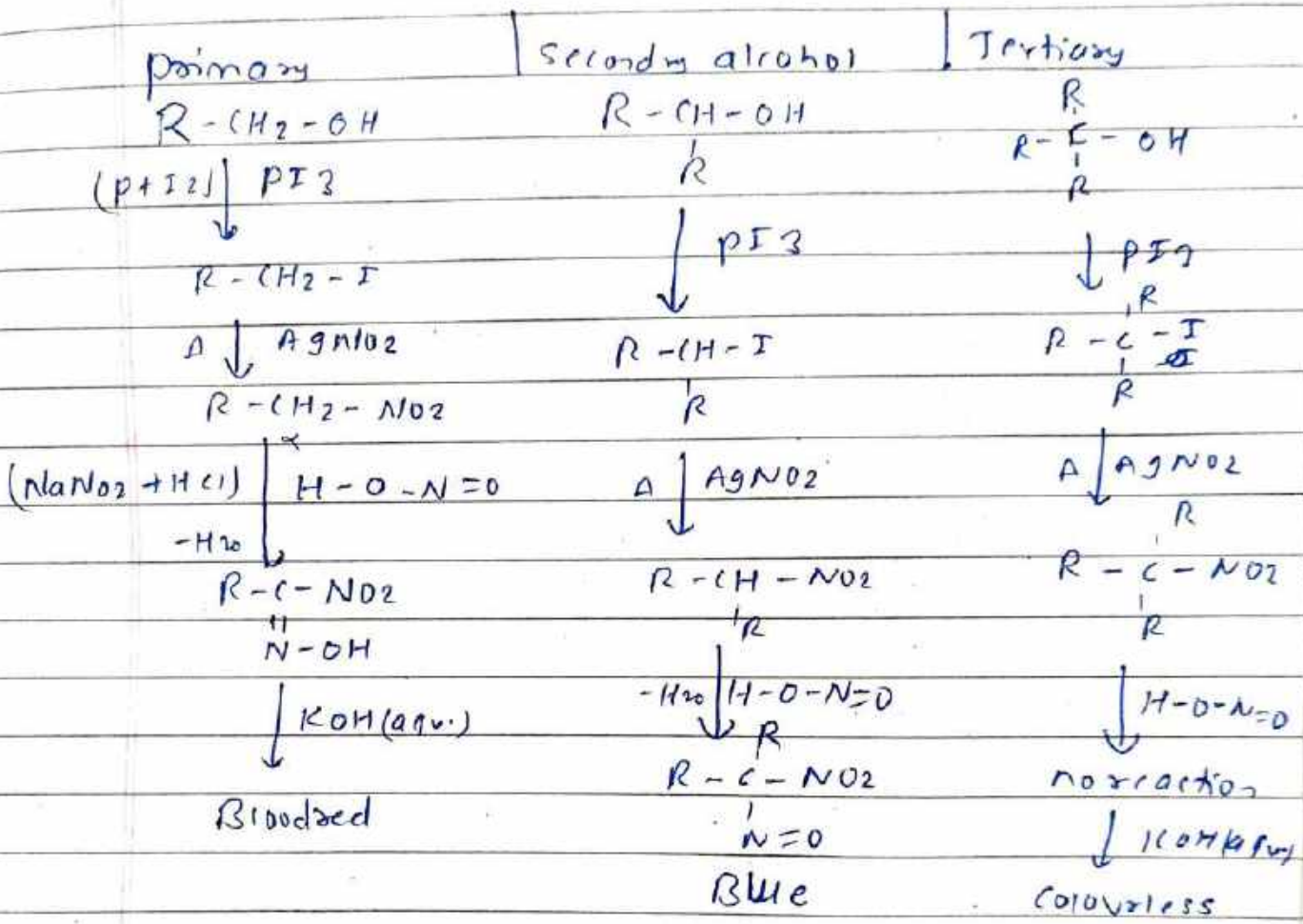
(3°)

→ But 3-alcohol does not under go dehydrogenation due to absence of α-hydrogen. But under same condition, it under goes intramolecular dehydration producing alkene.

VVI

Test reaction.

Distinction of 1, 2 and 3 - alcohol by victor mayer's method.



To distinguish primary, secondary, and tertiary alcohol by victor mayer's method, the alcohols are treated with phosphorous tri-iodide followed by treatment with silver nitrite. Then, they are treated with nitrous acid.

Finally aqueous KOH solution is added to them. The reaction

mixture which changes to blood red colour confirms primary alcohol. The reaction mixture which changes to blue colour confirms secondry alcohol and the reaction mixture which remains colourless confirms tertiary alcohol.