Alcohols and phenols

Alcohols :⇒ organic compounds containg −OH as functional group are called alcohols. Its general formula is $C_nH_{2n+1}OH$ and is represented as ROH. where n = 1, 2, 3 ------

n = 1 CH_3-OH
Methyl alcohol

n = 2 C_2H_5OH
Ethyl alcohol

Alcohols are derivatives (hydroxy derivatives of alkanes and they are obtained by replacing −H atom/s of alkanes by −OH group/s

$$C_nH_{2n+2} \xrightarrow[+OH]{-H} C_nH_{2n+1}OH$$

$$\underset{\text{Alkane}}{R-H} \xrightarrow[+OH]{-H} \underset{\text{Alcohol}}{R-OH}$$

eg. $$\underset{\text{Methane}}{CH_4} \xrightarrow[+OH]{-H} \underset{\text{Methyl alcohol.}}{CH_3-OH}$$

Nomenclature of alcohols:-

Common system :⇒ In this system, name of alcohol is written as alkyl alcohol.

IUPAC system ⇒ In this system, name of alcohol is written as alkanol.

Classification of alcohols

Alcohols

- A. On the basis of no. of –OH groups present in alcohol molecule.
- B. On the basis of nature of C-atom attached (bonded) to –OH group (classification of monohydric alcohols)

A. On the basis of no. of –OH groups present in alcohol molecule :⇒

Alcohols are divided into the following classes / types.

1. Monohydric alcohols :⇒ Alcohols containing only one –OH group.

CH_3-OH | CH_3-CH_2-OH | $CH_3-CH_2-CH_2-OH$

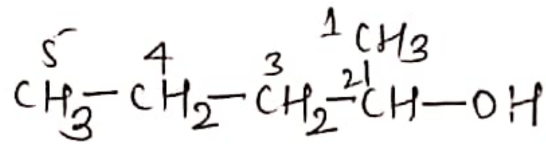
C.N. :⇒ Methyl alcohol | Ethyl alcohol | Propyl alcohol

I.N. :⇒ Methanol | Ethanol | Propanol

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

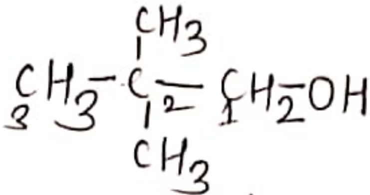
C.N. :⇒ Isopropyl alcohol | Isobutyl alcohol | sec-butyl alcohol

I.N. :⇒ Propane-2-ol or 2-Propanol | 2-Methylpropanol | Butan-2-ol



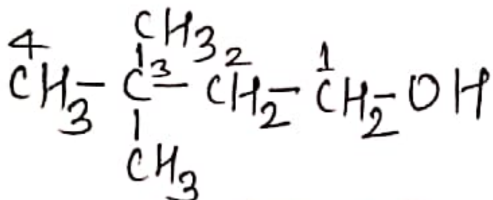
C·N ⇒ sec-pentyl alcohol

I·N· pentan-2-ol
or
2-pentanol



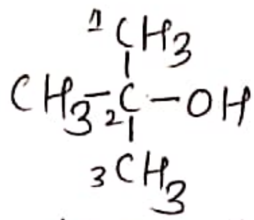
neopentyl alcohol

2,2-Dimethylpropanol



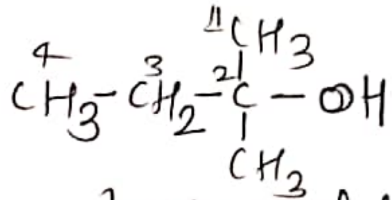
C·N ⇒ neohexyl alcohol

I·N ⇒ 3,3-Dimethylbutanol



tert-butyl alcohol

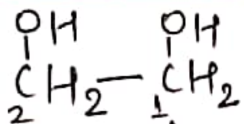
2-methylpropan-2-ol



tert-pentyl alcohol

2-methylbutan-2-o

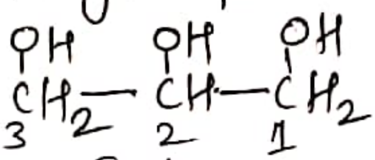
2· Dihydric alcohols :⇒ Alcohols containing two -OH groups.



C·N· ⇒ Ethylene glycol

I·N·⇒ Ethane-1,2-diol
or
1,2-Ethanediol·

3· Trihydric alcohols :⇒ Alcohols containing three -OH groups.



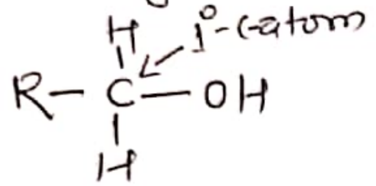
C·N·⇒ Glycerol

I·N·⇒ propane-1,2,3-triol
or
1,2,3-propanetriol

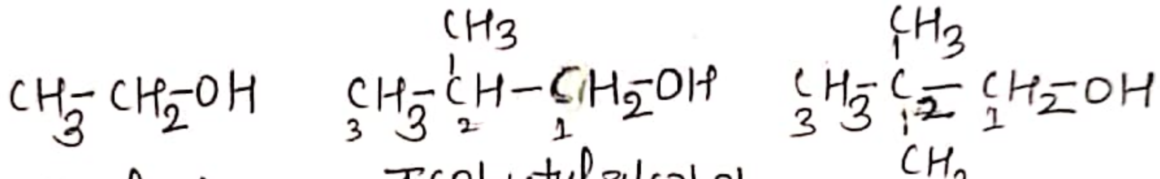
B. On the basis of nature of C-atom attached to -OH group
(Classification of monohydric alcohols)

Alcohols are of three types. i.e

1. Primary alcohol (1°-alcohol) :⇒ -OH group is attached to primary (1°)-carbon atom, the alcohol is called primary (1°) alcohol.

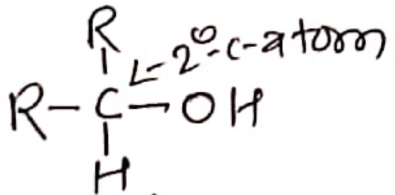


Functional group :- $-CH_2OH$



C.N. ⇒	Ethyl alcohol	Isobutyl alcohol	neopentyl alcohol
I.N. ⇒	Ethanol	2-Methylpropanol	2,2-Dimethylpropanol

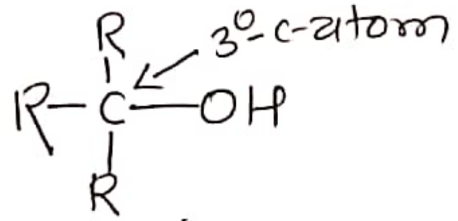
2. Secondary alcohol (2°-alcohol) :⇒ -OH group is attached to secondary (2°) carbon atom. The alcohol is called secondary (2°) alcohol.



Functional group :- >CHOH

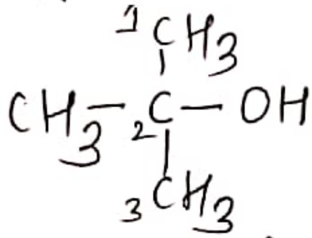
C.N ⇒	Isopropyl alcohol	sec-butyl alcohol
I.N. ⇒	propan-2-ol	Butan-2-ol

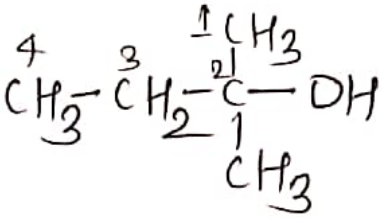
3. Tertiary alcohol (3°-alcohol) :⇒ −OH group is attached to tertiary (3°) carbon atom, the alcohol is called tertiary (3°) alcohol.



Functional group :- >C-OH

egs.





C.N. ⇒ tert-butyl alcohol   tert-pentyl alcohol

I.N. ⇒ 2-Methylpropan-2-ol   2-Methylbutan-2-ol

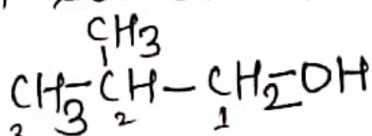
Isomerism in alcohols ⇒

Alcohols exhibit (show) three types of structural isomerism.

(i) chain isomerism :⇒ Alcohols containing at least four carbon atoms show chain isomerism.

$C_4H_{10}O$

$CH_3-CH_2-CH_2-CH_2-OH$ Butanol



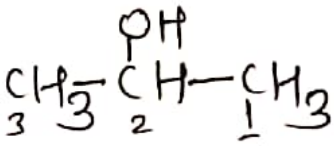
2-Methylpropanol

└ chain isomers ┘

(ii) position isomerism :⇒ Alcohols containing at least three carbon atoms show position isomerism.

C_3H_8O

$\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-OH$ propan-1-ol



propan-2-ol

└ position isomers ┘

3. Functional isomerism ⇒ Alcohols containing at least two carbon atoms show functional isomerism.

C_2H_6O	CH_3-CH_2-OH	$CH_3-OH-CH_3$
	Ethanol	Methoxymethane

└ Functional isomers ┘

Distinction between primary (1°), secondary (2°) and tertiary (3°) alcohols by victor Meyer's method:

The following steps are involved for the distinction between primary (1°), secondary (2°) and tertiary (3°) alcohols by victor-Meyer's method:

Step(I):- The given alcohol is first converted into iodoalkane (alkyl iodide) by treating it with cold HI or mixture of red phosphorus and iodine (P_4+I_2)

Step(II):- The formed iodoalkane is then converted into nitroalkane by treating it with $AgNO_2$ (silver nitrite) solution.

Step(III):- So the formed nitroalkane is treated with HNO_2 (nitrous acid) [i.e. $NaNO_2+HCl$]

Primary nitroalkane gives nitrolic acid, secondary nitroalkane gives pseudonitrol and tertiary nitroalkane doesnot respond with nitrous acid (HNO_2).

Step(IV):→ Now, the resulting solution is made alkaline by adding aq. KOH or NaOH and the colour of solution is observed.

- Blood red colouration indicates the presence of 1°-alcohol, blue colouration of indicates the presence of 2°-alcohol and no colouration (colourless) indicates the presence of 3°-alcohol.

Reagent	primary alcohol (1°-alcohol)	secondary alcohol (2°-alcohol)	Tertiary alcohol (3°-alcohol)
i) cold HI or P_4+I_2	$R-CH_2-OH$ ↓ cold HI $R-CH_2-I$	R_2CH-OH ↓ cold HI R_2CH-I	R_3C-OH ↓ cold HI R_3C-I
ii) $AgNO_2$	↓ $AgNO_2$ $R-CH_2-NO_2$	↓ $AgNO_2$ R_2CH-NO_2	↓ $AgNO_2$ R_3C-NO_2
iii) HNO_2 ($NaNO_2$+HCl)	↓ O=N-OH $R-C(=N-OH)-NO_2$ Nitrolic acid	↓ HO-N=O $R_2C(N=O)-NO_2$ Pseudonitrol	↓ HNO_2 No reaction
iv) aq.KOH	↓ aq.KOH Blood red	↓ aq.KOH Blue	↓ aq.KOH colourless

Q.1. Write down the isomeric alcohols of C_3H_8O and distinguish them by victor meyer's method

Q.2. Write down the isomeric alcohols of $C_4H_{10}O$ and distinguish them by victor-meyer's method.

General methods of preparation of monohydric alcohols:⇒

1. From haloalkane (alkyl halide) :⇒

When primary haloalkane (alkyl halide) is treated (heated) with aq. KOH or NaOH or moist silver oxide (Ag_2O), primary alcohol is formed.

$$R-X + KOH_{(aq)} \xrightarrow{\Delta} ROH + KX$$

Alkyl halide (1°) → Alcohol (1°)

eg. $CH_3-CH_2-I + KOH_{(aq)} \xrightarrow{\Delta} CH_3-CH_2-OH + KI$

Ethyl iodide → ethyl alcohol

$$R-X + AgOH \xrightarrow{\Delta} ROH + AgX \quad [Ag_2O + H_2O \rightleftharpoons 2AgOH]$$

Alkyl halide (moist silver oxide) → Alcohol

eg. $CH_3-CH_2-I + AgOH \xrightarrow{\Delta} CH_3-CH_2-OH + AgI$

ethyl iodide → ethyl alcohol.

Note:⇒ This method is not suitable for preparation of 2° and 3° alcohols because 2° haloalkane on hydrolysis aq. KOH or NaOH gives rise to a mixture of alcohol and alkene while 3° haloalkane gives alkene as the major product.

$$2CH_3-\underset{}{\overset{X}{\overset{|}{C}}}H-CH_3 + 2KOH_{(aq.)} \xrightarrow{\Delta} CH_3-\overset{OH}{\overset{|}{C}}H-CH_3 + CH_3-CH=CH_2 + KX + HX$$

2-Halopropane (2° haloalkane) → propan-2-ol (2° alcohol) + KX ; propene + HX

$$CH_3-\overset{X}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3 + KOH_{(aq.)} \xrightarrow{\Delta} CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2 + KX + H_2O$$

tert-butyl halide (2-Halo-2-methyl propane) 3° haloalkane → 2-methyl propene

2. From primary amine ⇒

When primary amine is treated with HNO_2 (nitrous acid) [$NaNO_2$ + HCl dil] at low temperature (<10°C) primary amine is obtained.

$$NaNO_2 + HCl \xrightarrow{<10°C} HNO_2 + NaCl$$

$$\underset{1°\text{-amine}}{R-NH_2} + \underset{\text{nitrous acid}}{HNO_2} \xrightarrow{<10°C} \underset{1°\text{-alcohol}}{R-OH} + N_2\uparrow + H_2O$$

(HO–N=O)

e.g. $$\underset{\text{ethylamine}}{CH_3-CH_2-NH_2} + HNO_2 \xrightarrow{<10°C} \underset{\text{ethyl alcohol}}{CH_3-CH_2-OH} + N_2 + H_2O$$

Note ⇒ Secondary and tertiary amines react with nitrous acid to form different products. So this method is not suitable for the preparation of secondary and tertiary alcohols.

$$\underset{\substack{\text{Diethylamine} \\ (2°\text{ amine})}}{C_2H_5-\overset{H}{\overset{|}{N}}-C_2H_5} + \underset{\text{nitrous acid}}{HNO_2} \longrightarrow \underset{\text{Diethyl-N-nitroamine}}{C_2H_5-\overset{C_2H_5}{\overset{|}{N}}-N=O} + H_2O$$

$$\underset{\text{Triethyl amine}}{C_2H_5-\overset{C_2H_5}{\overset{|}{N}}-C_2H_5} + \underset{\text{nitrous acid}}{HNO_2} \longrightarrow \underset{\text{Triethyl ammonium nitrite.}}{\left[C_2H_5-\overset{C_2H_5}{\overset{|}{\underset{\underset{H}{|}}{N}}}-C_2H_5\right]^+ N\bar{O}_2}$$

- In case of methyl amine, methyl nitrite is formed instead of methyl alcohol.

$$\underset{\text{methyl amine}}{CH_3NH_2} + HNO_2 \longrightarrow \underset{\text{methyl nitrite}}{CH_3-NO_2} + NH_3$$

3. From esters:- By hydrolysis of esters

When ester is hydrolysed in presence of mineral acid (HCl or H_2SO_4) or alkali (NaOH), alcohol is formed.

$$R-\overset{O}{\overset{\|}{C}}-OR' + H-OH \xrightarrow{dil.HCl,\ \Delta} R-\overset{O}{\overset{\|}{C}}-OH + R'OH$$

Ester → carboxylic acid + alcohol

e.g. $$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + H-OH \xrightarrow[\Delta]{dil.HCl} CH_3-\overset{O}{\overset{\|}{C}}-OH + C_2H_5OH$$

ethyl acetate → Acetic acid + ethyl alcohol

$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + NaOH \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-ONa + C_2H_5OH$$

ethyl acetate → Sodium acetate + ethyl alcohol.

Industrial preparation of alcohols:-

1. By 'oxoprocess':-

In this process, alkene reacts with a mixture of carbon monoxide and hydrogen i.e water gas $[CO+H_2]$ in the presence of cobalt carbonyl i.e $[Co(CO)_4]_2$ as catalyst under high pressure and temperature to yield an aldehyde which on catalytic hydrogenation with H_2/Ni gives primary alcohol (1° alcohol).

$$R-CH=CH_2 + [CO+H_2] \xrightarrow[\text{high press}^r,\ \text{temp}^r]{[Co(CO)_4]_2} R-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{H_2/Ni} R-CH_2-CH_2-CH_2-OH$$

Alkene + water gas → Aldehyde → primary alcohol

e.g. $$CH_2=CH_2 + [CO+H_2] \xrightarrow[\text{high press}^r,\ \text{temp}^r]{[Co(CO)_4]_2} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{H_2/Ni} CH_3-CH_2-CH_2-OH$$

ethylene (ethene) + water gas → propionaldehyde (propanal) → propyl alcohol (propanol) 1° alcohol.

$$CH_3-CH=CH_2 + [CO+H_2] \xrightarrow[\text{high press}^r,\ \text{temp}^r]{[Co(CO)_4]_2} CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{H_2/Ni} CH_3-CH_2-CH_2-CH_2-OH$$

propene → Butanal → Butanol (1° alcohol)

2. By fermentation of carbohydrates (sugar):-

The process of slow decomposition of large complex organic molecules into simpler ones in the presence of enzyme (biocatalyst) is called fermentation. By this process, Cane sugar (sucroses, maltose, glucose, fructose etc are converted into ethyl alcohol.

Ethanol (ethyl alcohol) is prepared on industrial scale by fermentation of sugar (molasses) and starch.

a) Ethanol from molasses (sucrose):-

The mother liquor obtained after the crystallization of sugar is called molasses, which contains 40 to 50% of sugar, mostly sucrose.

In this fermentation process, sucrose is converted into glucose and fructose in presence of enzyme invertase.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

The formed glucose or fructose is converted into ethyl alcohol in the presence of enzyme zymase.

$$\underset{\text{glucose or fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{ethyl alcohol}}{C_2H_5OH} + 2CO_2$$

The fermentation process gets completed in about 5 days (or 2-3 days). The fermented liquor obtained by this process is called wash (wort) which contains 8-10% ethanol. 95.6% ethanol is obtained by fractional distillation of the fermented liquor (wash) is called rectified spirit.

b) Ethanol from starch

Starch is converted into maltose in the presence of enzyme diastase.

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{diastase} nC_{12}H_{22}O_{11}$$

starch — maltose

The formed maltose is converted into glucose in the presence of enzyme maltase.

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

maltose — glucose

So the formed glucose is converted into ethyl alcohol in the presence of enzyme zymase.

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

glucose — ethyl alcohol.

3. By hydroboration-oxidation of ethene (Alkene) ⇒

Alkene reacts with diborane (B_2H_6) to form trialkyl borane which on oxidation with alkaline hydrogen peroxide (H_2O_2) gives alcohol.

Step I :- Hydroboration

$$>C=C< + B_2H_6 \text{ or } (BH_3)_2 \longrightarrow (-\underset{H}{\overset{|}{C}}-\overset{|}{\underset{|}{C}}-)_3B$$

Alkene — diborane — trialkylborane

Step-II :- oxidation

$$(-\underset{H}{\overset{|}{C}}-\overset{|}{\underset{|}{C}}-)_3B + 3H_2O_2 \xrightarrow{OH^{\ominus}} 3\,-\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- + B(OH)_3 \text{ or } H_3BO_3$$

Trialkyl borane. — hydrogen peroxide — Alcohol eg.:- $6CH_2=CH_2 + (BH_3)_2 \xrightarrow{\text{Hydroboration}} 2(CH_3-CH_2)_3B$

ethene, $(BH_3)_2$ or B_2H_6 → Triethylborane

$(CH_3-CH_2)_3B + 3H_2O_2 \xrightarrow{\text{Oxidation}} 3CH_3-CH_2-OH + B(OH)_3$

Triethylborane → ethyl alcohol

Note:- In case of unsymmetrical alkene, B-atom adds to C-atom having greater number of H-atoms i.e. antimarkovnikov's addition.

$CH_3-CH=CH_2 + (BH_3)_2 \longrightarrow (CH_3-CH_2-CH_2)_3B$

propene (Unsymmetrical alkene), $(BH_3)_2$ or B_2H_6 → Tripropylborane

$(CH_3-CH_2-CH_2)_3B + 3H_2O_2 \xrightarrow{OH^-} 3CH_3-CH_2-CH_2-OH + B(OH)_3$

propyl alcohol

Q. Identify (X) and (Y) in the following reaction.

$CH_3-CH_2-CH=CH_2 \xrightarrow{B_2H_6} (X) \xrightarrow{H_2O_2/OH^-} (Y)$.

⇒ $CH_3-CH_2-CH=CH_2 \xrightarrow{B_2H_6} (CH_3-CH_2-CH_2-CH_2)_3B \xrightarrow{H_2O_2/OH^-} CH_3-CH_2-CH_2-CH_2-OH$

Butene → Tributylborane (X) → Butyl alcohol (Butanol) (Y)

Definition of some common terms:-

Absolute alcohol:- 100% pure ethyl alcohol (ethanol) is called absolute alcohol.

Power alcohol:- A mixture of 80% petrol and 20% absolute ethyl alcohol with co-solvent benzene is called power alcohol. It is used as motor fuel.

Methylated spirit (Denatured alcohol) :- Ethyl alcohol containing 5 to 10% methyl alcohol is called methylated spirit. It is unfit for drinking purposes. It is poisonous in nature due to presence of methyl alcohol. It is also called denatured alcohol.

Rectified spirit :- A mixture of ethyl alcohol (95.87%) and water (4.13%) mixture is known as rectified spirit.

Alcoholic beverages :-

Those beverages which contain ethyl alcohol as the principal intoxicating agent are called alcoholic beverages. Alcoholic beverages are of two types:-
i.e. i) Undistilled alcoholic beverages.
ii) Distilled alcoholic beverages.

(i) Undistilled alcoholic beverages :-

Those beverages which are prepared by the fermentation of fruit juices and contain 3 to 20% of ethyl alcohol are called called undistilled alcoholic beverages. eg. wine, beer.

(ii) Distilled alcoholic beverages :-

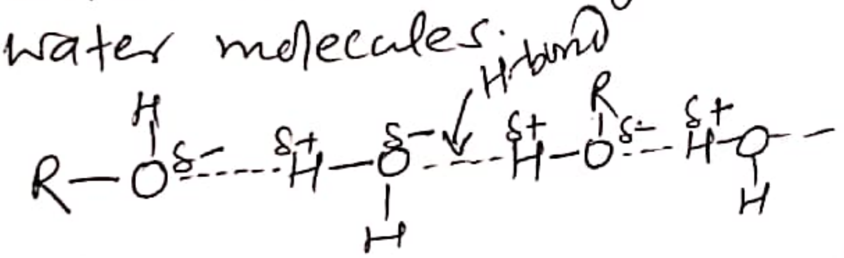
Those beverages which are prepared by the distillation of fermented liquor and contain about 40 to 50% of ethyl alcohol are called alcoholic beverages. eg. whisky, brandy, rum, gin, vodka etc.

Physical properties of monohydric alcohols:

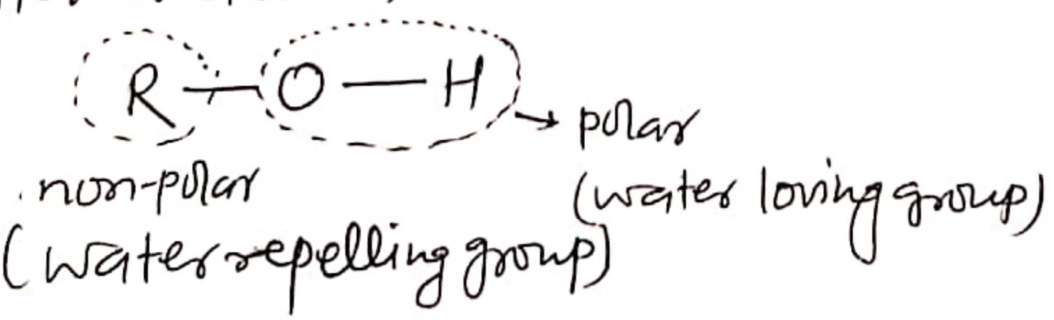
Physical properties:

State:- Lower members of alcohol upto C_{12} (ie $C_1 - C_{12}$) are colourless liquids and higher members having more than 12 carbon atoms (i.e. >12) are colourless and odourless waxy solids.
(Ethyl alcohol is a colourless and volatile liquid possessing a pleasant pungent smell and having a burning taste).

Solubility: Lower members of alcohols are highly soluble in water. This is due to the formation intermolecular hydrogen bonds between alcohol and water molecules.



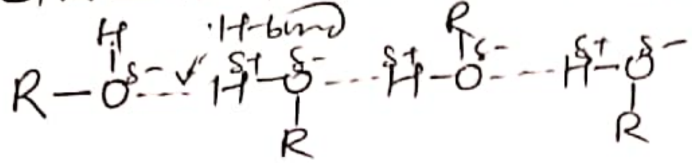
But solubility decreases with increasing molecular weight. As the molecular weight increases, the non-polar alkyl group becomes larger which acts as a water repelling group (i.e. prevents the formation of hydrogen bonds with water molecule.)



Boiling point:

Boiling pt. Alcohols

B.Pt. of alcohols are high due to the existence of intermolecular hydrogen bonds between the alcohol molecules.



Boiling point alcohols increases with increasing molecular mass.

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

methylalcohol, ethylalcohol, propylalcohol.

65°C, 78°C, 98°C

B.pt. increases →

For isomeric alcohols, B.Pt. of alcohols decreases with branching. As branching increases, surface area of molecule decreases (i.e. vanderwaal force of attraction decreases between the alcohol molecules).

$CH_3-CH_2-CH_2-CH_2OH > CH_3-CH_2-CH(OH)-CH_3 > CH_3-C(OH)(CH_3)-CH_3$

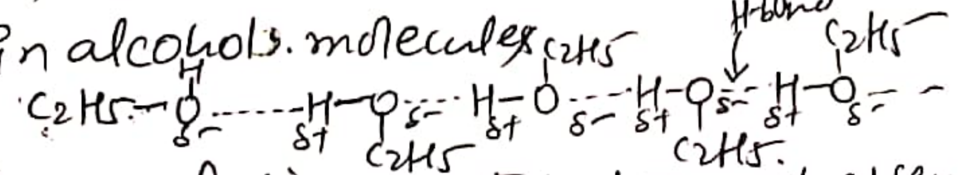
n-butylalcohol, sec-butylalcohol, tert-butyl alcohol

118°C, 99°C, 80°C

B.pt. decreases →

Q. Why is the boiling point of ethyl alcohol (ethanol) higher than that of dimethylether (methoxymethane)?

⇒ This is because of the existence of strong hydrogen bonding in alcohols molecules.



But incase of dimethylether, there is absense of H-bonds.

Reactivity of HX :- HI > HBr > HCl

Reaction of alcohols :- 3°-alcohol > 2°alcohol > 1°alcohol

$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}}}H-OH + HCl_{(g)} \xrightarrow[\Delta]{anh.ZnCl_2} CH_3-\overset{CH_3}{\overset{|}{C}}H-Cl + H_2O$$

Isopropyl alcohol (2°-alcohol) — conc. — isopropyl chloride

$$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH + HCl(g) \xrightarrow[\Delta]{anh.ZnCl_2} CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-Cl + H_2O$$

tert-butyl alcohol (3°-alcohol) — conc. — tert-butyl alcohol

⇒ Lucas reagent :⇒ anhydrous $ZnCl_2$ + conc. HCl

⇒ Reaction of 1° and 2° alcohols with HCl gas in presence of anh. $ZnCl_2$ is called Groove's method

b. With Phosphorus halide (PX_3 or PCl_5) :⇒

Ethyl alcohol reacts with phosphorus halide to form ethyl halide.

i) with PX_3 (PCl_3, PBr_3, PI_3) :⇒ to form ethyl halide along with phosphorous acid.

$$CH_3-CH_2-OH + PX_3 \longrightarrow CH_3-CH_2-X + H_3PO_3$$

ethyl alcohol — phosphorus trihalide — ethyl halide — phosphorous acid

$PX_3 = PCl_3$, PBr_3 or PI_3

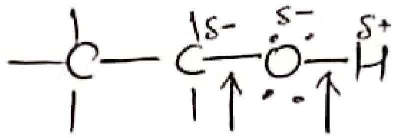
Since PBr_3 and PI_3 are unstable. so they are prepared in situ by the action of red phosphorus on Br_2 or I_2.

$$2P + 3X_2 \longrightarrow 2PX_3$$

X = Br or I

Chemical properties of monohydric alcohols (ethanol)

The structure of alcohol can be represented as,



cleavage takes place here.

The C–O and O–H bonds in alcohol molecule are polar in nature due to high electronegativity of O-atom. Besides this, O-atom of the –OH group has two unshared pair of electrons.

The chemical reactions of alcohols can be categorised into three types. i.e.

1. Reactions involving the cleavage of C–O bond.
2. Reactions involving the cleavage of O–H bond.
3. Reactions involving both alkyl group and hydroxyl group (i.e. Reactions involving the unshared pair electrons on O-atom).

1. Reactions involving the cleavage of C–O bond:-

a. with HX (halogen acid / hydrogen halide) :- Basic nature of alcohol.

When ethyl alcohol is heated with hydrogen halide in the presence of anhydrous $ZnCl_2$, ethyl halide is formed. where anh. $ZnCl_2$ acts as dehydrating agent.

$$\underset{\text{ethyl alcohol}}{CH_3-CH_2-OH} + \underset{\text{halogen acid}}{HX} \xrightarrow[\Delta]{anh.\,ZnCl_2} \underset{\text{ethyl halide}}{CH_3-CH_2-X} + H_2O$$

HX = HCl, HBr or HI

ii) With PCl_5 (Phosphorus pentachloride) :⇒ to form ethylchloride along with phosphorus oxychloride (phosphoryl chloride).

$$CH_3-CH_2-OH + PCl_5 \longrightarrow CH_3-CH_2-Cl + POCl_3 + HCl$$

ethyl alcohol → ethylchloride, Phosphoryl chloride

c) With $SOCl_2$ (thionyl chloride) :⇒

Ethyl alcohol reacts with $SOCl_2$ (thionylchloride) in the presence of pyridine to yield ethyl chloride.

$$CH_3-CH_2-OH + SOCl_2 \xrightarrow{pyridine} CH_3-CH_2-Cl + SO_2 + HCl$$

ethyl alcohol → ethyl chloride

2. Reactions involving the cleavage of O-H bond :

a) With reactive metals (alkali metals) like Na, K, Li :⇒

Ethyl alcohol reacts with reactive metals like Na, K, Li to form ~~Metal ethoxide~~ (metal alkoxide) and liberate hydrogen gas.

$$2\,CH_3-CH_2-OH + 2Na \longrightarrow 2\,CH_3-CH_2-ONa + H_2\uparrow$$

ethyl alcohol → Sodium ethoxide

$$2\,CH_3-CH_2-OH + K \longrightarrow 2\,CH_3-CH_2-OK + H_2\uparrow$$

ethyl alcohol → potassium ethoxide

Q. Why is sodium metal not stored in ethylalcohol (alcohol)?

at 140°c :⇒ to form diethyl ether (ethoxyethane)

$$CH_3-CH_2-OH + H-HSO_4 \xrightarrow{100^\circ c} CH_3-CH_2-HSO_4 + H_2O$$
(conc)

$$CH_3-CH_2-HSO_4 + H-O-CH_2-CH_3 \xrightarrow{140^\circ c} CH_3-CH_2-O-CH_2-CH_3 + H_2SO_4$$

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

ethyl alcohol → diethylether

at 170°c :⇒ to form ethylene (ethene)

$$CH_3-CH_2-OH + H-HSO_4 \xrightarrow{100^\circ c} CH_3-CH_2-HSO_4 + H_2O$$
(conc.)

$$\underset{H}{CH_2}-\underset{HSO_4}{CH_2} \xrightarrow{170^\circ c} CH_2=CH_2 + H_2SO_4$$

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

ethyl alcohol → ethylene

Note:-

1°-alcohol:- $CH_3-CH_2-OH \xrightarrow[170-180^\circ c]{95\%\ H_2SO_4} CH_2=CH_2 + H_2O$

ethyl alcohol → ethylene

2°-alcohol: $CH_3-CH_2-\underset{}{\overset{OH}{CH}}-CH_3 \xrightarrow[100^\circ c]{60\%\ H_2SO_4} CH_3-CH=CH-CH_3$ rather than $CH_3-CH_2-CH=CH_2$

sec-butyl alcohol → 2-Butene (rather than 1-butene)

3°-alcohol: $CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_3 \xrightarrow[80-90^\circ c]{20\%\ H_2SO_4} CH_2=C(CH_3)_2$

isobutylene

Imp b) With carboxylic acid (Esterification process or reaction)
(acetic acid)

When ethyl alcohol is heated with acetic acid (carboxylic acid) in the presence of conc. H_2SO_4, ethyl acetate (ester having fruity smell) is formed. This reaction is known as esterification reaction.

$$CH_3-CH_2-O\,H + HO-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\Delta]{conc.\,H_2SO_4} CH_3-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O$$

ethyl alcohol — acetic acid — ethyl acetate (ethyl ethanoate) fruity smell

The formed ester can be hydrolysed to give back acid and alcohol. Conc. H_2SO_4 being a dehydrating agent drives the reaction towards the forward direction.

3. Reactions involving both alkyl group and hydroxyl group (Reactions involving the unshared pair of electrons on O-atom):

a) Dehydration of alcohols :⇒

i) With conc. H_2SO_4 :⇒ Ethyl alcohol reacts with conc. H_2SO_4 (dehydrating agent) to form different products.

at 100°c :⇒ to form ethyl hydrogen sulphate

$$CH_3-CH_2-OH + H\,HSO_4 \xrightarrow{100°C} CH_3-CH_2-HSO_4 + H_2O$$

ethyl alcohol — conc. — ethyl hydrogen sulphate

ii) With Al_2O_3 (alumina) :⇒

Ethyl alcohol reacts with Al_2O_3 (dehydrating agent) to form different products:

at 250°c :⇒ to form diethylether (ethoxyethane)

$$2\,CH_3-CH_2-OH \xrightarrow[250^\circ C]{Al_2O_3} CH_3-CH_2-O-CH_2-CH_3 + H_2O$$

ethyl alcohol → diethylether

at 350°c :⇒ to form ethylene (ethene)

$$CH_3-CH_2-OH \xrightarrow[350^\circ C]{Al_2O_3} CH_2=CH_2 + H_2O$$

ethyl alcohol → ethylene

> Note:- order of ease of dehydration of alcohols:
>
> 3° alcohol > 2° alcohol > 1° alcohol > CH_3OH

b) Oxidation of primary, secondary and tertiary alcohols with mild oxidizing agents like acidified or alkaline $KMnO_4$ or acidified $K_2Cr_2O_7$:⇒

Primary and secondary alcohols are easily oxidised but tertiary alcohol is oxidised at vigorous condition (drastic condition).

Oxidation of primary alcohol :⇒

Primary alcohol is oxidised to an aldehyde which on further oxidation gives carboxylic acid.

$$CH_3-CH_2-OH + [O] \xrightarrow[-H_2O]{K_2Cr_2O_7/H^{\oplus} \text{ or } K_2Cr_2O_7 + dil \cdot H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{[O]} CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Ethyl alcohol (1^o-alcohol) → acetaldehyde (ethanal) → acetic acid (ethanoic acid)

oxidation of secondary alcohol :⇒

Secondary alcohol is oxidised to a ketone.

$$CH_3-\overset{OH}{\overset{|}{C}H}-CH_3 + [O] \xrightarrow[-H_2O]{K_2Cr_2O_7 + dil \cdot H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

Isopropyl alcohol (propan-2-ol) 2^o-alcohol → Acetone (propan-2-one)

oxidation of tertiary alcohol :⇒

Tertiary alcohol is oxidised to ketone under vigorous condition.

$$CH_3-\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3 + [O] \xrightarrow[\text{higher tempr (vigorous condition)}, -CO_2, -H_2O]{K_2Cr_2O_7 + H_2SO_4(conc)} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

tert-butyl alcohol (2-Methyl propan-2-ol) 3^o-alcohol → Acetone (propan-2-one)

This reaction is useful in the distinction of 1^o, 2^o and 3^o-alcohols.

Note :⇒ sec. alcohol on oxidation gives ketone which on further oxidation at vigorous condition to give carboxylic acids.

$$CH_3-\overset{OH}{\overset{|}{C}H}-CH_3 + [O] \xrightarrow[-H_2O]{K_2Cr_2O_7/H^{\oplus}} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{vigorous condition}]{[O]} CH_3-\overset{O}{\overset{\|}{C}}-OH + H-\overset{O}{\overset{\|}{C}}-OH$$

isopropyl alcohol (2^o-alcohol) → Acetone → acetic acid + formic acid tertiary alcohol on oxidation at vigorous condition gives ketone which on further oxidation to give carboxylic acids and finally give CO_2 and H_2O.

$$CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_3 \xrightarrow{H^{\oplus}} \left[CH_3-\underset{CH_3}{C}=CH_2 \right] \xrightarrow[\text{vigorous condition}]{[O]} \underset{\text{Acetone}}{(CH_3)_2C=O} + HCOOH$$

tert-butyl alcohol (3° alcohol) → isobutylene

$$\underset{\text{Acetone}}{(CH_3)_2C=O} \xrightarrow[\text{vigorous condition}]{[O]} \underset{\text{Acetic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{formic acid}}{H-\overset{O}{\overset{\|}{C}}-OH}$$

$$HCOOH \xrightarrow{[O]} CO_2 + H_2O$$

[Carboxyl group goes with smaller alkyl group]

c) catalytic dehydrogenation of 1° and 2° alcohols and dehydration of 3° alcohol ⇒

When vapours of alcohols are passed over heated copper (as catalyst) at 300°C, they form different products. Primary alcohol gives aldehyde and secondary alcohol gives ketone with the liberation of H_2 (dehydrogenation) while tertiary alcohol gives alkene with the formation of water molecule (dehydration) [due to absence of α-hydrogen tertiary alcohol gives alkene].

$$CH_3-CH_2-OH \xrightarrow{Cu,\ 300°C} CH_3-\overset{O}{\overset{\|}{C}}-H + H_2\uparrow$$

ethyl alcohol (ethanol) 1° alcohol → Acetaldehyde (ethanal)

$$CH_3-\overset{OH}{CH}-CH_3 \xrightarrow{Cu,\ 300°C} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_2\uparrow$$

isopropyl alcohol (propan-2-ol) 2° alcohol → Acetone (2-propanone)

$$CH_3-\underset{CH_3}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-CH_3 \xrightarrow{Cu,\ 300^\circ C} CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2 + H_2O$$

tert-butyl alcohol (2-Methylpropan-2-ol) 3°-alcohol → isobutylene (2-Methylpropene)

This reaction is useful in distinction of 1°, 2° and 3°-alcohols

Laboratory tests of ethanol (ethyl alcohol):

(I) Iodoform test:

When ethanol solution is warmed (at $60^\circ C$) with iodine crystals (or solution) and dil. NaOH or KOH (alkali), a yellow ppt. of is obtained. This reaction is known iodoform.

$$CH_3-CH_2-OH + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\text{Iodoform (Yellow ppt)}}{CHI_3\downarrow} + HCOONa + 5NaI + 5H_2O$$

ethyl alcohol (ethanol)

$$2NaOH + I_2 \xrightarrow{\Delta} \underset{\text{Sodium hypoiodite}}{NaOI} + NaI + H_2O\ ] \times 4$$

i) Oxidation of ethanol

$$CH_3-CH_2-OH + NaOI \xrightarrow{\Delta} \underset{\text{acetaldehyde}}{CH_3-\overset{O}{\overset{||}{C}}-H} + NaI + H_2O$$

ii) Iodination of acetaldehyde

$$CH_3-\overset{O}{\overset{||}{C}}-H + 3NaOI \xrightarrow{\Delta} \underset{\text{Tri-iodo acetaldehyde (iodal)}}{CI_3-\overset{O}{\overset{||}{C}}-H} + 3NaOH$$

iii) Hydrolysis of triiodoacetaldehyde

$$CI_3-\overset{O}{\overset{||}{C}}-H + NaOH \xrightarrow{\Delta} CHI_3 + HCOONa$$

Net reaction: $CH_3-CH_2-OH + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3\downarrow + HCOONa + 5NaI + 5H_2O$

Note:⇒ Iodoform test is given by alcohols containing $CH_3-\overset{OH}{\overset{|}{C}}H-$ group

In case primary alcohol, only ethyl alcohol (CH_3-CH_2-OH) gives iodoform test.

In case of Isopropyl alcohol (secondary alcohol):⇒

$$CH_3-\overset{OH}{\overset{|}{C}}H-CH_3 + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3\downarrow + CH_3-\overset{O}{\overset{||}{C}}-ONa + 5NaI + 5H_2O$$

Isopropyl alcohol (propan-2-ol) 2°-alcohol; iodoform

In case acetaldehyde (Ethanal) : Aldehyde.

$$CH_3-\overset{O}{\overset{||}{C}}-H + 3I_2 + 4NaOH \xrightarrow{\Delta} CHI_3\downarrow + H-\overset{O}{\overset{||}{C}}-ONa + 3NaI + 3H_2O$$

Acetaldehyde (Ethanal); iodoform

In case of acetone (propanone): ketone

$$CH_3-\overset{O}{\overset{||}{C}}-CH_3 + 3I_2 + 4NaOH \xrightarrow{\Delta} CHI_3\downarrow + CH_3-\overset{O}{\overset{||}{C}}-ONa + 3NaI + 3H_2O$$

Acetone (2-propanone); iodoform

Note:⇒ Iodoform test is given by aldehyde or ketone containing $CH_3-\overset{O}{\overset{||}{C}}-$ group

(II) Ester test:⇒

Ethyl alcohol is heated with acetic acid (carboxylic acid) in the presence of conc. H_2SO_4 to form ethyl acetate (ester having fruity smell). This reaction is known is esterification.

$$CH_3-CH_2-OH + HO-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{conc.\,H_2SO_4} CH_3-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O$$

ethyl alcohol (ethanol) Acetic acid (ethanoic acid ethyl acetate (ethyl ethanoate) fruity smell.