ALCOHOLS

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B.sc Part ll

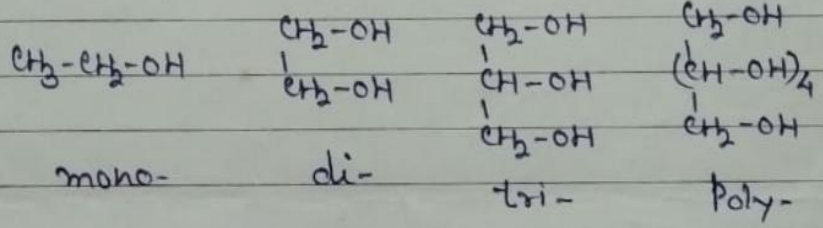
Second Paper.

ALCOHOLS

Alcohols are compounds in which a hydroxyl gp (-OH) is attached to saturated carbon atom.

(R-OH)

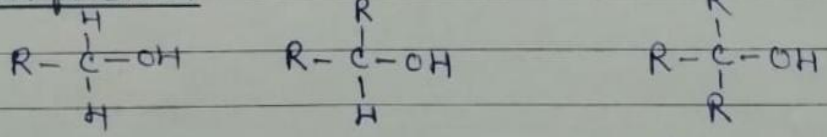
Alcohols are classified as mono-, di-, tri-, & poly-hydric alcohols according to the number of hydroxyl gps.



mono- di- tri- Poly-

Monohydric alcohols:

Classification:

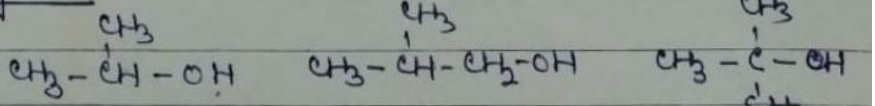


1° (Pri) 2° (Sec) 3° (Ter)

Nomenclature:

By three systems →

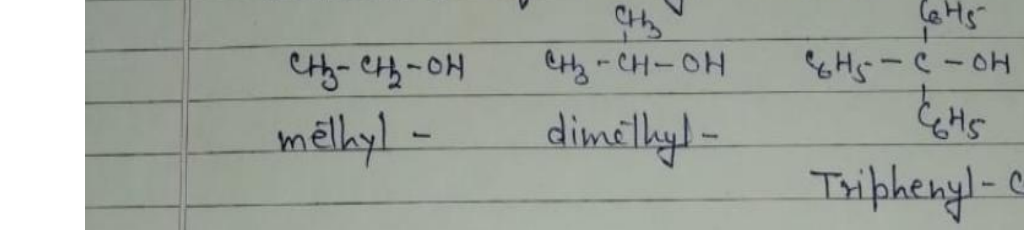
① Common system →



isopropyl- (2°) isobutyl (1°) t-butyl alc (3°)

② Carbinol System :

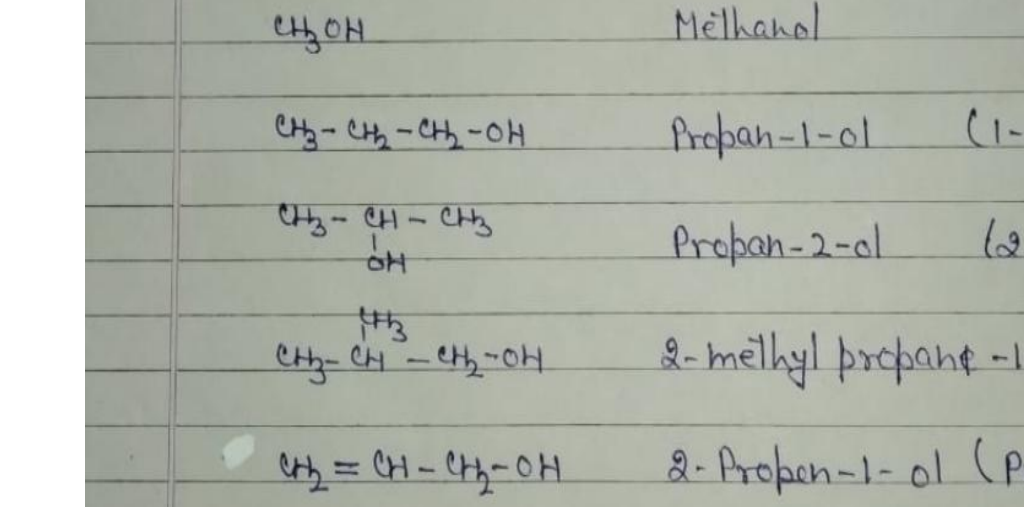
methyl alcohol is known as Carbinol. In this system alcohols are considered as derivatives of methyl alcohol.



methyl - dimethyl - Triphenyl-carbinol.

③ IUPAC system :

alkane ↔ 'e' replace frome -'ol' ↔ alkanol



CH_3OH Methanol

$CH_3-CH_2-CH_2-OH$ Propan-1-ol (1-Propanol)

Propan-2-ol (2-Propanol)

2-methyl propane-1-ol

$CH_2=CH-CH_2-OH$ 2-Propen-1-ol (Prop-2-ene-1-ol)

Methods of formation :

① Reduction of aldehydes & ketones :

aldehydes give — 1° alcohol

ketones " — 2° alcohol if they reduced by - (a) Catalytic hydrogenation (Ni, Pt, Pd, Ru)

or by - (b) metal solvent (Na · ethanol)

or by - (c) complex metal hydride ($LiAlH_4$, $NaBH_4$) (LAH)

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Page No.
Exp. No

$R-CHO \xrightarrow[\text{Na-ethanol [H] or } NaBH_4 \text{ or } LiAlH_4]{Ni \text{ or } Pt \text{ or } Pd \text{ or } Ru/H_2 \text{ or}} R-CH_2-OH$

$\begin{matrix} R \\ R' \end{matrix}\!\!>C=O \xrightarrow[\text{Na-ethanol [H] or } NaBH_4 \text{ or } LiAlH_4]{Ni \text{ or } Pt \text{ or } Pd/H_2 \text{ or}} \begin{matrix} R \\ R' \end{matrix}\!\!>CH-OH$

② Reduction of carboxylic acids :

$-COOH$ reduced to -1°-alcohols.

(a) $R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[H_3O^+]{LiAlH_4 \,/\, \text{dry ether}} R-CH_2-OH \quad (1^{\circ})$

$C_6H_5-\overset{O}{\overset{\|}{C}}-OH \longrightarrow C_6H_5-CH_2-OH \quad (1^{\circ})$

(b) $3 \cdot R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{B_2H_6} 3\,R-CH_2-OH \quad (1^{\circ})$

③ Reduction of esters :

(a) $R-\overset{O}{\overset{\|}{C}}-OR'$ (acyl part / Alkoxy part) $\xrightarrow[\text{Bouveault-Blanc red.}]{Na \,/\, C_2H_5-OH} R-CH_2-OH + R'-OH$

$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \longrightarrow CH_3-CH_2-CH_2-CH_2OH + C_2H_5OH$

(b) $R-\overset{O}{\overset{\|}{C}}-OR \xrightarrow[H_3O^+]{LiAlH_4 \,/\, \text{dry ether}} R-CH_2-OH + R'-OH$

Hydrogen bonding :

The O-H bond of alcohols is highly polar because oxygen is electronegative. The polarity of O-H bond gives rise to forces of attraction between a $+\delta$ positive Hydrogen in one

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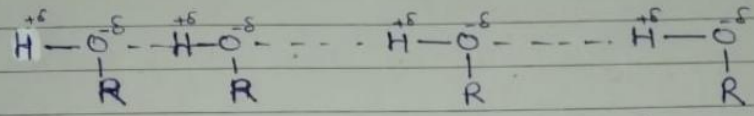
molecule & partially negative oxygen in other molecule. These forces of attraction are referred to as H-bonding. This is the reason that alcohols have higher boiling point. Due to hydrogen bonding alcohols exist as associated molecules.



Intermolecular H-bonding.

(A compound that forms hydrogen bonds between its own molecules can also form hydrogen bonds with water. These alcohol-water hydrogen bonds are the cause of high solubility of lower alcohols in water. In higher alcohols, the nonpolar alkyl group become more imp. They have less tendency to form hydrogen bonds with water & hence are less soluble.)
(Solubility increases with increase in branching of higher alcohols)

Reactions of alcohols:

① Reaction with metals: (O–H)

Alcohols react with Na or K to form alkoxides with the liberation of Hydrogen gas.

$$2\ R\text{–}OH + 2\ Na \longrightarrow 2\ R\text{–}O^{-}Na^{+} + H_2$$

$$6\ (CH_3)_3C\text{–}OH + 2\ Al \longrightarrow 2\left[(CH_3)_3CO\right]_3Al + 3\ H_2$$

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The above reaction shows that alcohols are acidic in nature. The reason for this is that the O–H bond in alcohols is polar & allows the release of the hydrogen atom as proton (H^+). Acidic nature of alcohols is due to the -ve charge of the oxygen atom.

Alcohols are weak acids than water due to inductive effect (e releasing) of alkyl gp.

CH_3-OH > Primary > Sec > tert

CH_3-OH > $R-CH_2-OH$ > $\begin{matrix} R \\ R \end{matrix}\!\!>\!CH-OH$ > $\begin{matrix} R \\ R \\ R \end{matrix}\!\!>\!C-OH$

(2) Reaction with G.Rs :

Alcohols react with G.R.s ($RMgX$) to form alkanes.

$$R'-OH + RMgX \longrightarrow RH + R'OMgX$$

$$CH_3CH_2-OH + CH_3MgBr \longrightarrow CH_4 + CH_3-CH_2-OMgBr$$

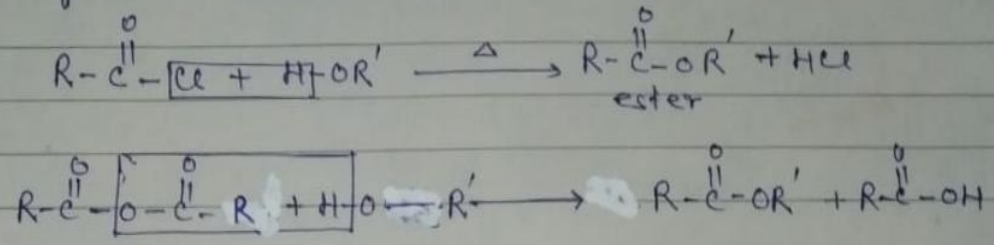
(3) Reaction with carboxylic acids :

Alcohols react with carboxylic acids to form esters. Conc. H_2SO_4 is used as a catalyst.

$$R'-OH + HO-\overset{O}{\overset{\|}{C}}-R \longrightarrow R'-O-\overset{O}{\overset{\|}{C}}-R$$ ester

(4) Reaction with acid halides & acid anhydrides :

Alcohols react with acid halides & acid anhydrides to form esters.



⑤ Reaction with Hydrogen Halides : (R–OH)

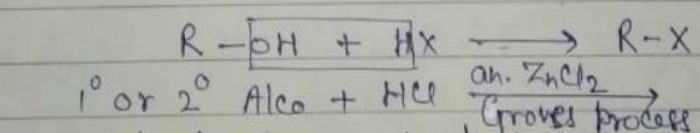
Alcohols react with hydrogen halides (HX) to form the corresponding alkyl halides. The order of reactivity of halogen acids is —

$$HI > HBr > HCl$$

- t- is most stable $x^{\oplus}$
- reaction stable $x^{\oplus}$?
- read ?

The order of reactivity of alcohols in these reactions is →

$$t > Sec > pri$$



No catalyst is required in the case of HBr & HI but $ZnCl_2$ (Anhydrous) is used in HCl.

⑥ Reaction with phosphorus halides :

Alcohols react with phosphorus pentahalides & trihalides to form alkyl halides.

$$R-OH + PX_5 \longrightarrow R-X + POX_3 + HX$$

$$3\,R-OH + PX_3 \longrightarrow 3\,R-X + H_3PO_3$$

⑦ Reaction with Thionyl chloride:

Alcohols react with Thionyl chloride to form alkyl chlorides.

$$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2\uparrow + HCl\uparrow$$

$$CH_3-CH_2-OH + SOCl_2 \longrightarrow CH_3-CH_2-Cl + SO_2\uparrow + HCl\uparrow$$

⑧ Oxidation:

Oxidation of alcohols can be used to distinguish p-, sec-, & t-alcohols.

- Primary alcohols oxidised to aldehydes & then to acids →

$$CH_3\cdot CH_2\cdot OH \xrightarrow[Na_2Cr_2O_7/H^+]{[O]} CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[Na_2Cr_2O_7/H^+]{[O]} CH_3-\overset{O}{\overset{\|}{C}}-OH$$

- Sec alcohols are oxidised to the corresponding ketones.

$$CH_3-\overset{OH}{\overset{|}{C}}H-CH_3 \xrightarrow[Na_2Cr_2O_7/H^+]{[O]} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

- t-alcohols $CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH \xrightarrow{\quad''\quad}$ No reaction

⑨ Reduction:

Alcohols undergo reduction with con HI & red phosphorus to produce alkanes.

$$R\text{-}OH + 2HI \xrightarrow[\Delta]{P} RH + I_2 + H_2O$$

$$CH_3\cdot CH_2\cdot OH + 2HI \longrightarrow CH_3\cdot CH_3 + I_2 + H_2O$$

⑩ Dehydrogenation:

- Primary alcohols lose hydrogen & give an aldehyde.

$$CH_3\cdot CH_2\cdot OH \xrightarrow[300^\circ C]{Cu} CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}H + H_2$$

- Sec alcohol lose hydrogen & yield a ketone.

$$CH_3\text{-}\overset{OH}{\overset{|}{C}}H\text{-}CH_3 \xrightarrow[300^\circ C]{Cu} CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + H_2$$

- 3-alcohols are not dehydrogenated but lose a molecule of water to give alkenes.

$$CH_3\text{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}\text{-}OH \xrightarrow[300^\circ C]{Cu} CH_3\text{-}\overset{CH_2}{\overset{\|}{\underset{CH_3}{\underset{|}{C}}}} + H_2O$$

— x —

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