ALKANOLS | ALCOHOLS | HYDROXY COMPOUNDS

They are compounds that contain 1 or more. OH group(s) linked to a Carbon atom

⇒ classification

(a) Based on number of OH groups

i) Monohydric alcohols/Aliphatic alcohols — they posses 1 ÷ OH group only.

General formula = $C_nH_{2n+1}OH$ = ROH

eg $\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_2OH$ (Propanol, straight chain)

$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H(\overset{1}{C}H_3)\overset{1}{C}H_2OH$ (2-Methylpentanol, branched)

They could be saturated/unsaturated

$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}(OH)-\overset{1}{C}H_3$ (Saturated), sp^3

Hexan-2-ol

$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}=\overset{2}{C}-\overset{1}{C}H_2$ (Hex-2-en-1-ol, Unsaturated) sp^2

OH

or (diols)

ii) Dihydric alcohols — bears 2-OH groups

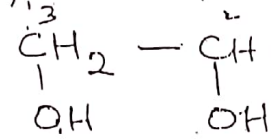
eg $\overset{4}{C}H_3\overset{3}{C}H(OH)-\overset{2}{C}H(OH)\overset{1}{C}H_3$ (Butan-2,3-diol)

A vicinal (vic-) diol: 2 adjacent C atoms

$H_3\overset{4}{C}-\overset{1}{C}(OH)_2-\overset{3}{C}H_2\overset{2}{C}H_3$ (Butan-2,2-diol)

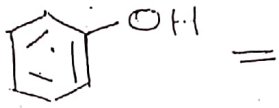
A Geminal (gem-) diol - OH on same C atom.

iii) Trihydric alcohols (Triols) — bears 3-OH group

e.g  Propane-1,2,3-triol (Glycerol)

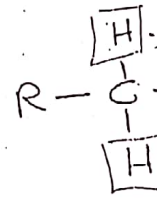
iv) Polyhydric alcohols (Polyols) > 3 OH groups.

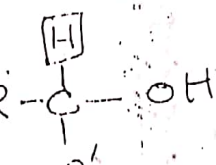
v) Aromatic alcohol — OH group is directly attached to a benzene ring (Ar) e.g C_6H_5OH

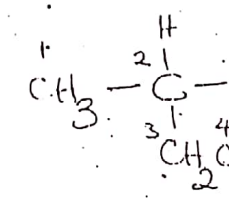
 = Phenyl alcohol
= Phenol

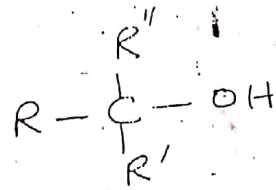
(B) Based on number of Hydrogens (alkyls) attached to the C bearing the -OH group (Most common to ROHs)

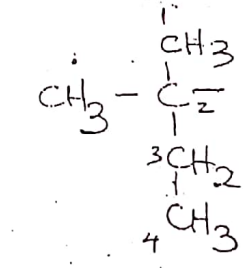
1° ⇒ (Primary) ⇒  Methyl
eg methanol


e.g ethanol, propanol, butanol etc

2° (Secondary) ⇒ 

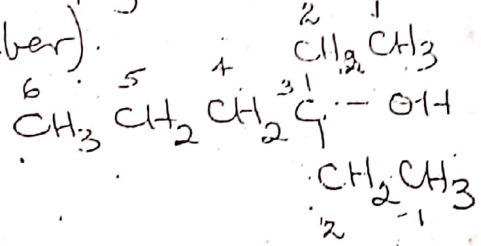
eg 
Butan-2-ol

3° (Tertiary) ⇒ 

eg 
2-Methylbutan-2-ol

⇒ Nomenclature

- Replace 'e' in alkane with 'ol' = alkanol.
- Position of -OH should be indicated (lowest possible number).



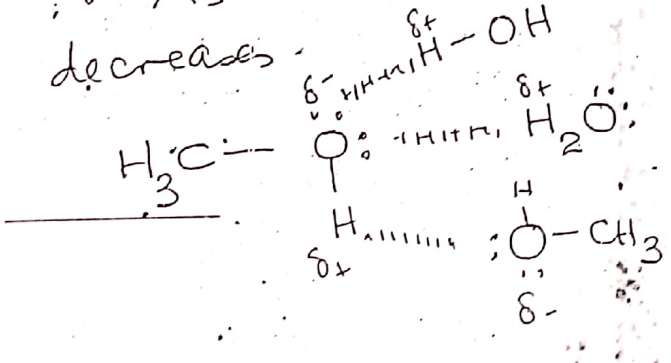
3-Ethylhexan-3-ol
(3° ROH)

⇒ Physical Properties

- Simple ROHs, eg CH_3OH, C_2H_5OH, propanol and butanol are liquids at room temperature; while higher ROHs are solids
- $C_1 - C_3$ ROHs are watersoluble, while $> C_3$ are insoluble/immiscible with H_2O. E.g Butanol is immiscible with water in all ratios.

This is because $C_1 - C_3$ ROHs can form hydrogen bond (H-bond) when dissolved in H_2O, while $> C_4$ ROHs do not.

∴ As RMM increases, solubility in water decreases.



---- H-bonds formed between CH_3OH & H_2O

Question Propanol is miscible with H_2O in all ratios, while butanol is not. Why?

- Boiling points of ROH is >> than those of their corresponding alkanes

CH_3OH = 64 – 65°C ≈ 32 g mol^{-1} / C_2H_6 = 30 g mol^{-1}, gas

C_2H_5OH = 78 °C ≈ 46 g mol^{-1} / C_3H_8 = 41 g mol^{-1}, gas

C_3H_7OH = 97°C = 60 g mol^{-1} / C_4H_{10} = 58 g mol^{-1}; liq 36°C

- Boiling point / melting points / density increases with increasing relative molecular mass, but decreases with increased branching.

CH_3OH = 65°C

C_2H_5OH = 78°C

C_3H_7OH = 97°C

C_4H_9OH = 118°C

Propanol = 97°C

Propan-2-ol = 87°C

Butanol = 118°C

2-Methylpropanol = 108°C

- In terms of isomeric alcohols, 1° > 2° > 3° ROH

1° $CH_3CH_2CH_2CH_2OH$ = 118°C Butanol

2° $CH_3CH_2\underset{OH}{C}HCH_3$ = 100°C Butan-2-ol

3° $CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_3$ = 83°C 2-Methylpropan-2-ol

- As number of OH group increases, bpt / Mpt / density increases

CH_3CH_2OH 78°C

$H_2C(OH)-CH_2(OH)$ 197°C

⇒ Chemical Properties

1) Combustion
Simple ROHs burn with a pale blue flame
→ CO_2 and H_2O

eg $C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$

2) Reaction with alkali metals
They react with metallic Na or K → an alkoxide/alkaneoxide (–OR) and $H_2\uparrow$

$2C_2H_5OH + 2Na_{(s)} \longrightarrow 2CH_3CH_2ONa + H_2\uparrow$
(Sodium ethoxide)

(3) Reaction with hydrogen halides (HCl, HBr, HI)

$ROH + HX \longrightarrow RX + H_2O$

1° $CH_3CH_2OH + HCl \xrightarrow[\text{reflux}]{ZnCl_2 \text{ catalyst}} CH_3CH_2Cl + H_2O$ (Brown ring)

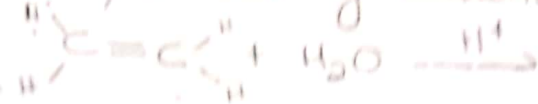
1° $CH_3CH_2OH + HBr \xrightarrow[\text{reflux}]{NaBr/\text{conc } H_2SO_4} CH_3CH_2Br + H_2O$ (Brown ring)

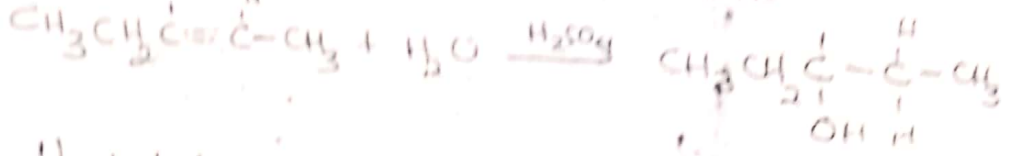
2° $CH_3\underset{\underset{OH}{|}}{CH}CH_3 + HCl \xrightarrow[\text{room temp}]{ZnCl_2 \text{ cat}} CH_3\underset{\underset{Cl}{|}}{CH}CH_3 + H_2O$ (Brown ring)

3° $CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + HCl \xrightarrow[\text{room temp}]{ZnCl_2} CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + H_2O$ (Brown ring)

Preparation

1) Hydration of alkenes (Markownikov's rule applies)



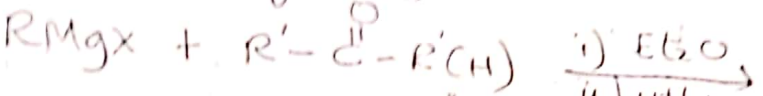


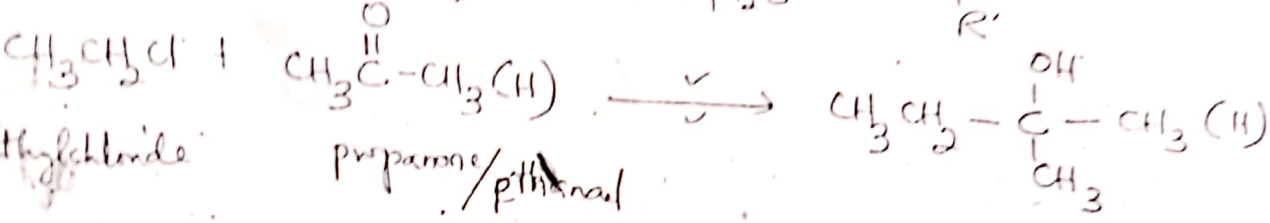
2) Hydrolysis of alkylhalides:

$$RX + H_2O \longrightarrow ROH + HX$$

$$CH_3CH_2Cl + H_2O \longrightarrow CH_3CH_2OH + HCl$$

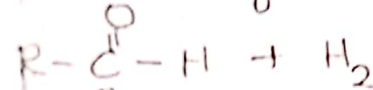
3) Reaction of RMgX with C=O compounds





Ethylchloride — propanone / pthanal

* Reduction of aldehydes & Ketones & Carboxylic acids



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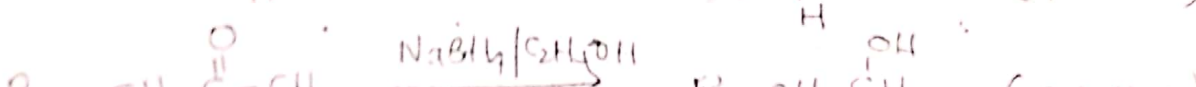

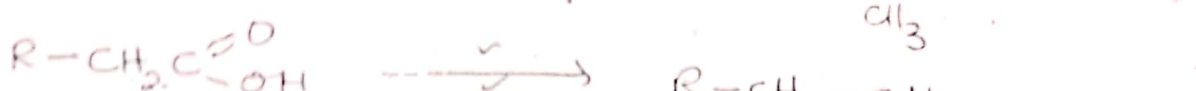

This is known as the LUCAS' Test and it is used for distinguishing between 1°, 2° & 3° ROH.

1° ROH — requires heating before the brown ring appears
2° ROH — No heating, takes place at room temp, but takes a longer time to yield the brown ring
3° ROH — requires no heating, takes place at room temp and generates the brown ring 'in situ' (on the spot).

④ Reaction with Phosphorous halides

Phosphorous trichloride, PCl_3 and phosphorous pentachloride, PCl_5 reacts with ROH ⟶ RX and $POCl_3$ | P_2O_3 | H_3PO_3.

$$3ROH + PX_3 \longrightarrow 3RX + H_3PO_3$$

phosphoric acid

$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$$

$$3CH_3CH_2OH + 2PCl_3 \longrightarrow 3CH_3CH_2Cl + P_2O_3 + HCl$$

$$3CH_3CH_2OH + PCl_3 \longrightarrow 3CH_3CH_2Cl + H_3PO_3$$ (slow reaction)

This is a qualitative test for the presence of OH group in an organic compound. ie white fumes of HCl.

(5) Oxidation

1° ROH $\xrightarrow{[O]}$ $RC(=O)H$ $\xrightarrow{[O]}$ $RC(=O)OH$

eg CH_3CH_2OH $\xrightarrow{[O]}$ $CH_3C(=O)H$ $\xrightarrow{[O]}$ $CH_3C(=O)OH$

Ethanal — Ethanal — Ethanoic acid

2° ROH $\xrightarrow{[O]}$ $RC(=O)R'$ $\xrightarrow{[O]}$ ✗ no visible reaction

$CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_3$ $\xrightarrow{[O]}$ $CH_3CH_2C(=O)CH_3$ $\xrightarrow{[O]}$ ✗ (Stable to oxidation)

Butan-2-ol — Butanone

3° ROH $\xrightarrow{[O]}$ ✗

$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$ $\xrightarrow{[O]}$ ✗ No visible reaction. Stable to oxidation.

2-Methylpropan-2-ol

eg. $[O]$ = oxidizing agents = $H^+/KMnO_4, \Delta$, $H^+/K_2Cr_2O_7, \Delta$

(6) Esterification

$R'OH + RC(=O)OH \rightleftharpoons RC(=O)OR' + H_2O$

eg $CH_3C(=O)OH + CH_3CH_2OH \rightleftharpoons CH_3C(=O)OCH_2CH_3 + H_2O$

Ethanoate — Ethyl

= Ethyl ethanoate

$CH_3CH_2C(=O)OH + CH_3CH_2OH \rightleftharpoons CH_3CH_2C(=O)OCH_2CH_3 + H_2O$

Propanoate — Ethyl

= Ethyl propanoate