ALKANOLS | ALCOHOLS
HYDROXY COMPOUNDS

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

⇒ <u>classification</u>

(A) ~~B~~ 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)

$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H(CH_3)\overset{1}{C}H_2OH$ (2-Methylpentanol, branched)

They could be saturated / unsaturated

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

$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}=\overset{2}{C}-\overset{1}{C}H_2OH$ (Hex-2-enol, Unsaturated) sp^2

~~Ex~~

ii) Dihydric alcohols (diols) — 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 different C atoms

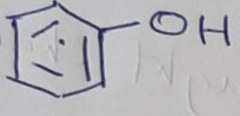
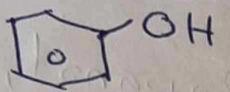
$H_3\overset{4}{C}-\overset{3}{C}-\overset{2}{C}(OH)_2-\overset{1}{C}H_3$ (Butan-2,2-diol)
A Geminal (gem-) diol - OH on same C atom.

iii) Trihydric alcohols (Triols) — bears 3 – OH groups

eg $\overset{3}{C}H_2 - \overset{2}{C}H - \overset{1}{C}H_2$ with OH on each carbon ($\underset{OH}{CH_2} - \underset{OH}{CH} - \underset{OH}{CH_2}$) Propane-1, 2, 3-triol (Glycerol)

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

v) Aromatic alcohols – OH group is directly attached to a benzene ring (Ar) eg C_6H_5OH

 =  = Phenyl alcohol = Phenol

⑤ Based on number of Hydrogens (alkyls) attached to the C bearing the –OH group (Most common to ROHs)

1° (Primary) ⇒ $\boxed{H} - \underset{\boxed{H}}{\overset{\boxed{H}}{C}} - OH$ Methyl alcohol eg methanol

$R - \underset{\boxed{H}}{\overset{\boxed{H}}{C}} - OH$ eg ethanol, propanol, butanol etc

2° (Secondary) ⇒ $R - \underset{R'}{\overset{\boxed{H}}{C}} - OH$ eg $\overset{1}{C}H_3 - \underset{\overset{3}{C}H_2\overset{4}{C}H_3}{\overset{H}{\overset{2}{C}}} - OH$

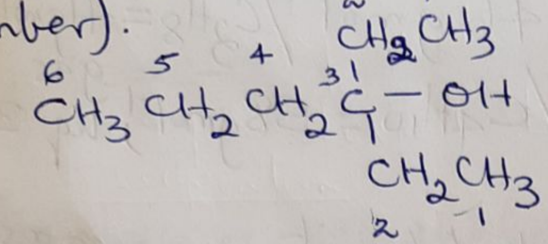
Butan-2-ol

3° (Tertiary) ⇒ $R - \underset{R'}{\overset{R''}{C}} - OH$ eg $CH_3 - \underset{{}^{3}CH_2 - {}_{4}CH_3}{\overset{{}^{1}CH_3}{\overset{2}{C}}} - OH$

2-Methylbutan-2-ol

⇒ Nomenclature

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

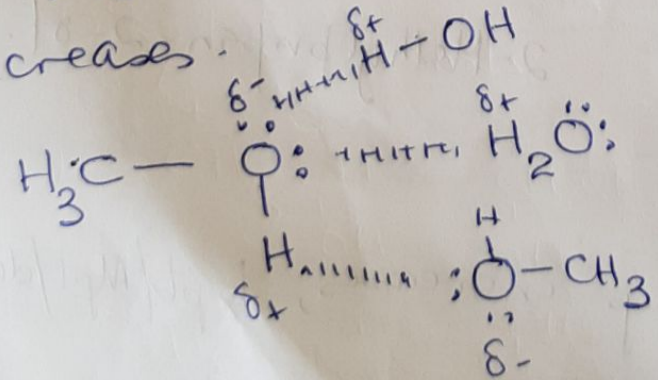


3-Ethylhexan-3-ol
(3° ROH)

⇒ Physical Properties

- Simple ROHs, eg CH_3OH, C_2H_5-OH, 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. Eg 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

<u>Question</u> 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

$CH_3OH = 64-65°C \doteq 32\,gmol^{-1} / C_2H_6 = 30\,gmol^{-1}$

$C_2H_5OH = 78°C = 46\,gmol^{-1} / C_3H_8 = 41\,gmol^{-1}$,

$C_3H_7OH = 97°C = 60\,gmol^{-1} / C_4H_{10} = 58\,gmol^{-1}$, gas liq 36°C

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

$CH_3OH = 65°C$	Propanol = 97°C
$C_2H_5OH = 78°C$	Propan-2-ol = 87°C
$C_3H_7OH = 97°C$	Butanol = 118°C
$C_4H_9OH = 118°C$	2-Methylpropanol = 108°C

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

1° $CH_3CH_2CH_2CH_2OH = 118°C$ Butanol

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

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

- As number of OH group increases, b pt / Mpt / density increases

CH_3CH_2OH 78°C

$\underset{OH}{\underset{|}{H_2C}} - \underset{OH}{\underset{|}{CH_2}}$ 197°C

Preparation

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

$$H_2C=CH_2 + H_2O \xrightarrow{H^+} -\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}$$

$$CH_3CH_2\overset{H}{C}=\overset{H}{C}-CH_3 + H_2O \xrightarrow{H_2SO_4} CH_3CH_2\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-CH_3$$

2) Hydrolysis of alkylhalides

$$Rx + H_2O \xrightarrow[\Delta]{} ROH + Hx$$

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

3) Reaction of RMgx with C=O compounds

$$RMgx + R'-\overset{O}{\overset{||}{C}}-R''(H) \xrightarrow[ii)\ H^+/H_2O]{i)\ Et_2O} R-\underset{R'}{\overset{OH}{C}}-R''(H)$$

$$CH_3CH_2Cl + CH_3\overset{O}{\overset{||}{C}}-CH_3(H) \xrightarrow[\checkmark]{\checkmark} CH_3CH_2-\underset{CH_3}{\overset{OH}{C}}-CH_3\ (H)$$

Ethylchloride propanone/ethanal

4) Reduction of aldehydes ~~&~~ Ketones & Carboxylic acids

$$R-\overset{O}{\overset{||}{C}}-H + H_2 \xrightarrow[\Delta]{Pd/Pt/Ni/Ru} RCH_2OH$$

eg ~~CH_3CH~~ eg $CH_3CH_2C\overset{O}{\underset{H}{}}$ $\xrightarrow[\checkmark]{\checkmark}$ $CH_3CH_2\underset{H}{\overset{OH}{C}}-H$ (1° ROH)

$$R-CH_2C\overset{O}{\underset{H}{}} \xrightarrow{LiAlH_4/Et_2O} R-CH_2\underset{H}{\overset{OH}{C}}-H \quad (1°\ ROH)$$

$$R-CH_2\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow{NaBH_4/C_2H_5OH} R-CH_2\underset{CH_3}{\overset{OH}{CH}} \quad (2°\ ROH)$$

$$R-CH_2C\overset{O}{\underset{OH}{}} \xrightarrow[\checkmark]{\checkmark} R-CH_2-\underset{OH}{CH_2} \quad (1°\ ROH)$$

⇒ 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/alkane oxide (–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° $CH_3\underset{\displaystyle OH}{\underset{|}{C}H}CH_3 + HCl \xrightarrow[\text{room temp}]{ZnCl_2 \text{ cat}} CH_3\underset{\displaystyle Cl}{CH}CH_3 + H_2O$

(Brown ring)

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

(Brown ring)

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 can be seen

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

$$3ROH + PX_3 \longrightarrow 3RX + \underset{\text{phosphoric acid}}{H_3PO_3}$$

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

$$3CH_3CH_2OH + 2PCl_3 \longrightarrow 3CH_3CH_2Cl + P_2O_3 + HCl$$ (slow reaction)

$$3CH_3CH_2OH + PCl_3 \longrightarrow 3CH_3CH_2Cl + H_3PO_3$$

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

(5) Oxidation

$$1°\ ROH \xrightarrow{[O]} RC\overset{=O}{\underset{-H}{}} \xrightarrow{[O]} RC\overset{=O}{\underset{-OH}{}}$$

eg $$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{[O]} \underset{\text{Ethanal}}{CH_3C\overset{=O}{\underset{-H}{}}} \xrightarrow{[O]} \underset{\text{Ethanoic acid}}{CH_3C\overset{=O}{\underset{-OH}{}}}$$

$$2°\ ROH \xrightarrow{[O]} RC\overset{=O}{\underset{-R'}{}} \xrightarrow{[O]} \times$$ no visible reaction

$$\underset{\text{Butan-2-ol}}{CH_3CH_2\underset{OH}{\underset{|}{C}}HCH_3} \xrightarrow{[O]} \underset{\text{Butanone}}{CH_3CH_2\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow{[O]} \times$$ (Stable to oxidation)

$$3°\ ROH \xrightarrow{[O]} \times$$

$$\underset{\text{2-methylpropan-2-ol}}{CH_3-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_3} \xrightarrow{[O]} \times$$ No visible reaction. Stable to oxidation

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

(6) Esterification

$$R'OH + RC\overset{=O}{\underset{-OH}{}} \rightleftharpoons RC\overset{=O}{\underset{-OR'}{}} + H_2O$$

eg $$CH_3C\overset{=O}{\underset{-OH}{}} + CH_3CH_2OH \rightleftharpoons \underbrace{CH_3\overset{O}{\overset{\|}{C}}}_{\text{ethanoate}}-O\underbrace{C_2H_5}_{\text{Ethyl}} + H_2O$$

= Ethyl ethanoate

$$CH_3CH_2C\overset{=O}{\underset{-OH}{}} + CH_3CH_2OH \rightleftharpoons \underbrace{CH_3CH_2\overset{O}{\overset{\|}{C}}}_{\text{Propanoate}}-O\underbrace{CH_2CH_3}_{\text{Ethyl}} + H_2O$$

= Ethyl propanoate