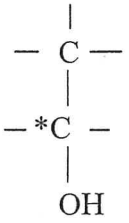
ALCOHOLS

→ All alcohols contain a (-OH) group.

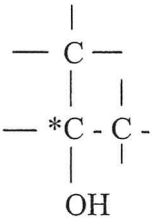
Classification

→ Alcohols can be classified as PRIMARY, SECONDARY or TERTIARY depending on the extent of carbon chain branching about the site of the OH group. A primary alcohol has only ***one*** carbon chain extension leading from the carbon to which the OH group is attached. A secondary alcohol has ***two*** carbon chain extensions leading from the carbon to which the OH group is attached while a tertiary alcohol is the most branched with ***three*** carbon chain extensions.

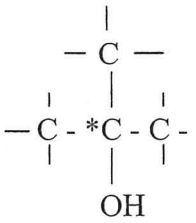
Primary (1°)



Secondary (2°)



Tertiary (3°)



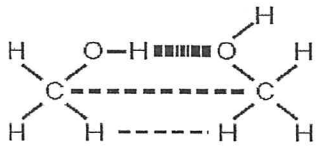
→ Because the site of OH group attachment in highly branched 3^0 alcohols are sometimes protected from attack by chemical reagents simply because of the bulkiness of the carbon chains. Tertiary alcohols are often less reactive as a result of this ***steric*** (geometric) ***hindrance***. Primary alcohols have their OH group at the end of a chain by definition and are the most reactive while secondary alcohols exhibit intermediate reactivity.

Physical Properties

1. Shorter chain alcohols are VOLATILE (easily evaporated) liquids. Their boiling points increase with size of chain. All alcohols are capable of exhibiting hydrogen bonding interactions due to the presence of the polar OH group, but as the length of carbon chain increases, the Dispersion forces rise leading to these increases in melting and boiling point. Longer chain alcohols may be greasy solids.

BOILING POINTS OF SOME ALCOHOLS

Number of carbon atoms	Name	Formula	Boiling point (°C)
1	Methanol	CH_3OH	65
2	Ethanol	CH_3CH_2OH	78
3	Propan-1-ol	$CH_3CH_2CH_2OH$	97
4	Butan-1-ol	$CH_3CH_2CH_2CH_2OH$	118



methanol—an alcohol

▮▮▮▮ hydrogen bonding
---- dispersion forces

2. Some alcohols will dissolve in water. The solubility decreases as the carbon chain length increases making the percentage polarity of the molecule too low to permit significant solute-solvent interactions. With longer chain alcohols the OH group becomes less significant and the molecules become more and more non-polar inhibiting their solubility in a polar solvent such as water. They may however become more soluble in non-polar solvents.

SOLUBILITY OF SOME ALCOHOLS IN WATER AT 25°C

Name	Formula	Solubility (mol per 100 g water)
Methanol	CH_3OH	Completely miscible
Ethanol	CH_3CH_2OH	Completely miscible
Propan-1-ol	$CH_3CH_2CH_2OH$	Completely miscible
Butan-1-ol	$CH_3CH_2CH_2CH_2OH$	0.11
Pentan-1-ol	$CH_3CH_2CH_2CH_2CH_2OH$	0.030
Hexan-1-ol	$CH_3CH_2CH_2CH_2CH_2CH_2OH$	0.0058
Heptan-1-ol	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$	0.00086
Octan-1-ol	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$	Completely immiscible

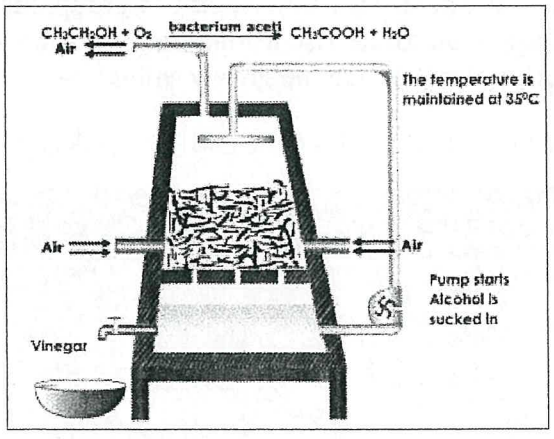
Preparation:

1. FERMENTATION

Yeast contains an enzyme that *CATALYSES the decomposition of GLUCOSE into CO_2 + ETHANOL (CH_3CH_2OH).

$$C_6H_{12}O_6 \xrightarrow{\text{yeast}} 2\,CH_3CH_2OH + 2CO_2$$

- A catalyst SPEEDS UP a chemical reaction without actually taking part!



2. FROM ETHENE

By acid catalysed (H_2SO_4) HYDRATION (addition of H_2O).

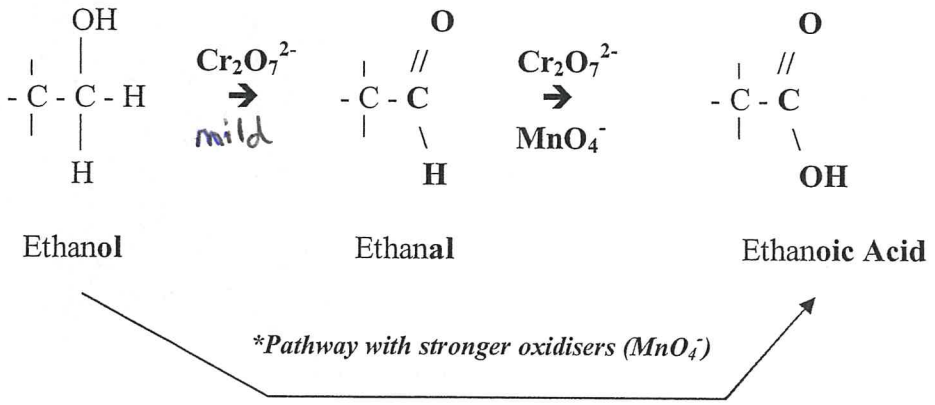
$$CH_2 = CH_{2(g)} + H_2O \xrightarrow[*\,H^+\ (H_2SO_4)]{\text{Acid}} CH_3 - CH_2OH \quad \text{Ethanol}$$

Reactions:

1. Oxidation of Alcohols

→ Alcohols are oxidised to differing degrees by laboratory oxidising agents. Permanganate is a more powerful oxidizer than dichromate and so the pathways for oxidation are different.

Primary (1°)



EXAMPLE 1:

The equation for the reaction of propan-1-ol with an acidified solution of potassium dichromate, to form propanal, is:

$$CH_3CH_2CH_2OH(l) \rightarrow CH_3CH_2CHO(l) + 2H^+(aq) + 2e^- \quad \times 3$$
$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) \quad \times 1$$

$$3CH_3CH_2CH_2OH(l) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3CH_3CH_2CHO(l) + 2Cr^{3+}(aq) + 7H_2O(l)$$

A clear orange solution is added to a clear and colourless liquid producing a clear green solution

EXAMPLE 2:

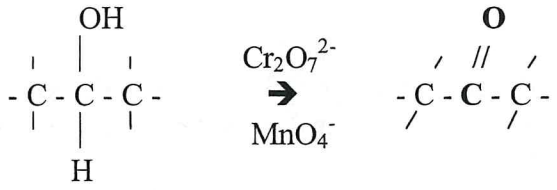
The equation for the preparation of propanoic acid from propan-1-ol, using acidified potassium permanganate solution is:

$$CH_3CH_2CH_2OH(l) + H_2O(l) \rightarrow CH_3CH_2COOH(l) + 4H^+(aq) + 4e^- \quad \times 5$$
$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l) \quad \times 4$$

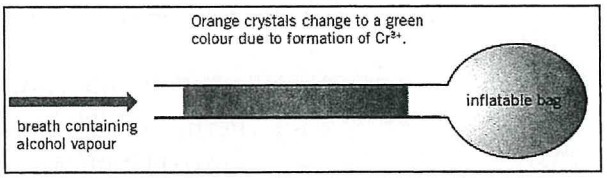
$$5CH_3CH_2CH_2OH(l) + 4MnO_4^-(aq) + 12H^+(aq) \rightarrow 5CH_3CH_2COOH(l) + 4Mn^{2+}(aq) + 11H_2O(l)$$

A clear purple solution was added to a clear and colourless liquid. The solution decolourises immediately to a clear and colourless solution.

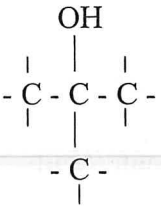
Secondary (2°)



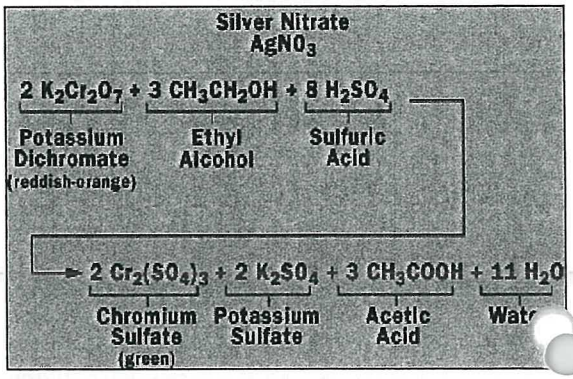
Propan-2-ol Propanone (Propan-2-one)



Tertiary (3°)



→ **NO REACTION**



2-Methylpropan-2-ol or 2-Methyl-2-propanol

EXAMPLE 3:

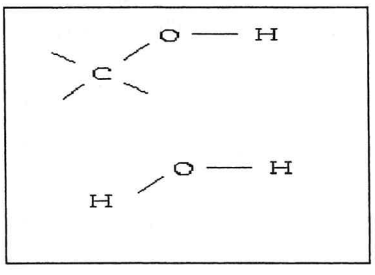
$CH_3CH(OH)CH_2CH_3(l) \rightarrow CH_3COCH_2\ CH_3(l) + 2H^+(aq) + 2e^-$ × 5

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ × 2

$5CH_3CH(OH)CH_2CH_3(l) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 5CH_3COCH_2CH_3(l) + 2Mn^{2+}(aq) + 8H_2O(l)$

A clear purple solution was added to a clear and colourless liquid. The solution decolourises immediately to produce a bi-layer with a clear and colourless liquid on top of a clear and colourless solution.

2. Reaction with Alkali Metals : (Extension)



→ Alcohols can react with Alkali metals such as Na liberating H_2.

$2\ CH_3 - OH + 2Na \rightarrow 2CH_3O^- + Na^+ + H_2\uparrow$

Sodium **Methoxide**

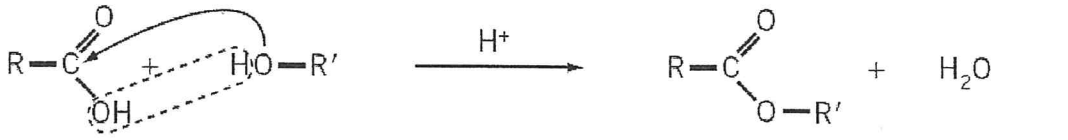
* (Alkoxide)

→ These reactions are very similar to the reaction of Na and H_2O and are used to identify alcohol structures. The reaction rate is far faster for primary alcohols than secondary and in turn tertiary alcohols!

3. ESTERIFICATION :

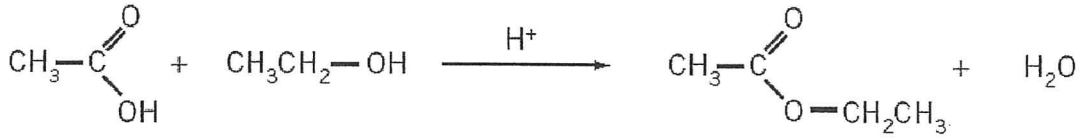
→ Alcohols can react with carboxylic acids and form a linked molecule known as an **ESTER**.

1.



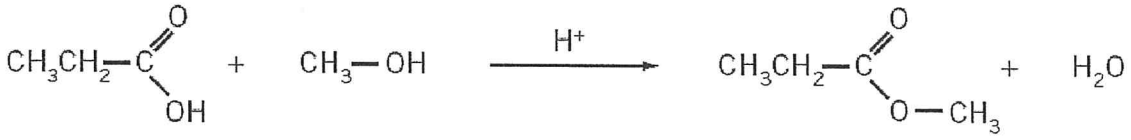
carboxylic acid alcohol ester

2.



ethanoic acid ethanol ethyl ethanoate

3.



propanoic acid methanol methyl propanoate

EXAMPLE :

$$CH_3COOH_{(l)} + CH_3CH_2OH_{(l)} \xrightarrow{H^+ / \text{Catalyst}} CH_3COOCH_2CH_3{}_{(l)} + H_2O_{(l)}$$

(Ethyl Ethanoate)

A clear and colourless liquid is added to another clear and colourless liquid producing a fruity smelling, clear and colourless liquid.

(May mention a bi-layer as the ester would float on whatever water is exuded in the reaction)