Alcohols

a recall the chemistry of alcohols, exemplified by ethanol, in the following reactions: ☐

(i) combustion

(ii) substitution to give halogenoalkanes

(iii) reaction with sodium

(iv) oxidation to carbonyl compounds and carboxylic acids

(v) dehydration to alkenes

(vi) formation of esters by esterification with carboxylic acids

(vii) formation of esters by acylation with acyl chlorides using ethyl ethanoate and phenyl benzoate as examples

b (i) classify hydroxy compounds into primary, secondary and tertiary alcohols ☐

(ii) suggest characteristic distinguishing reactions, e.g. mild oxidation

c deduce the presence of a CH3CH(OH)– group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodomethane ☐

ALCOHOLS

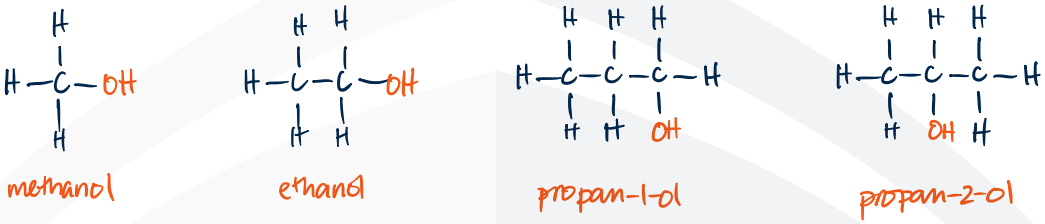
17.1 Alcohols	a)	recall the chemistry of alcohols, exemplified by ethanol, in the following reactions:
		(i) combustion
		(ii) substitution to give halogenoalkanes
		(iii) reaction with sodium
		(iv) oxidation to carbonyl compounds and carboxylic acids
		(v) dehydration to alkenes
		(vi) formation of esters by esterification with carboxylic acids
		(vii) formation of esters by acylation with acyl chlorides using ethyl ethanoate and phenyl benzoate as examples
	b)	(i) classify hydroxy compounds into primary, secondary and tertiary alcohols
		(ii) suggest characteristic distinguishing reactions, e.g. mild oxidation
	c)	deduce the presence of a $CH_3CH(OH)$– group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodomethane

ALCOHOLS

The simplest alcohols form a homologous series of **general formula $C_nH_{2n+1}OH$ –** *provided there are no rings.*

Named as substituted alkanes by removing the final –e and adding –ol

For isomers the position of the OH is given by a number – *propan-1-ol and propan-2-ol*

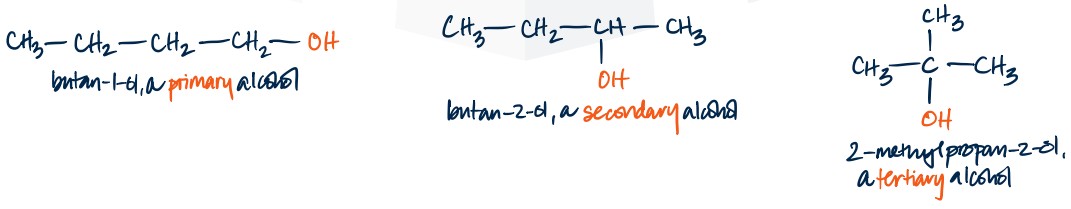


1

ALCOHOLS

The —OH group is called the hydroxyl group. When drawing alcohols always make sure the bond goes to the O.

The functional group, however, is referred to as primary/secondary/tertiary alcohol as chemical behavior of alcohols, especially with oxidation, often depends on the structure of the alcohol.



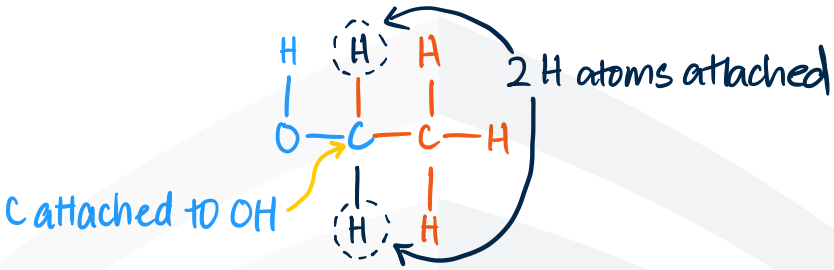
Alcohols may be described as primary, secondary or tertiary, depending on the number of H atoms attached to the carbon with the –OH group on it.

2

PRIMARY ALCOHOLS

Ethanol is a primary alcohol, as it has two hydrogens attached to the C with the –OH attached.

A primary alcohol thus contains the **–CH_2OH group**.

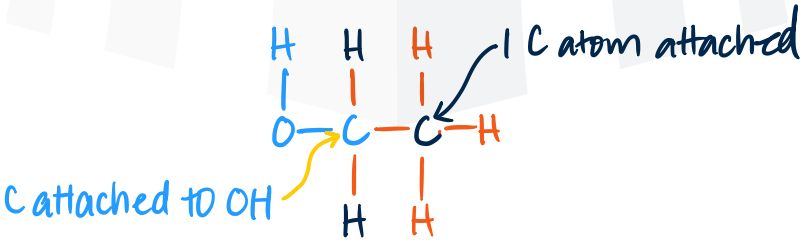


3

PRIMARY ALCOHOLS

Another way of looking at this is that the C with the –OH attached has one other C attached to it.

One C attached = primary.

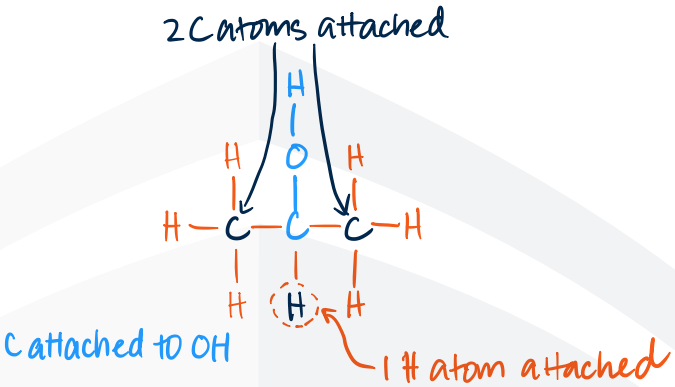


4

SECONDARY ALCOHOLS

Propan-2-ol is a secondary alcohol, as it has one H atom attached to the C with the –OH attached.

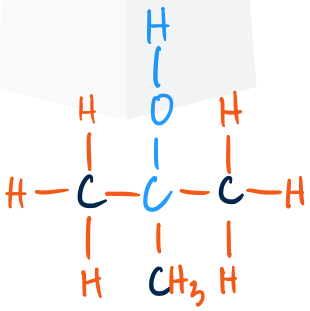
A secondary alcohol contains the **–CHOH** group.



5

TERTIARY ALCOHOLS

2-methylpropan-2-ol is a tertiary alcohol, as there are no H atoms (or three C atoms) attached to the C with the –OH attached.



6

PROPERTIES

Alcohols are useful solvents and are key intermediates in the production of esters, which are important solvents for the paints and plastics industries.

The polar —OH group readily forms hydrogen bonds to similar groups in other molecules.

This accounts for the following major differences between the alcohols and the corresponding alkanes.

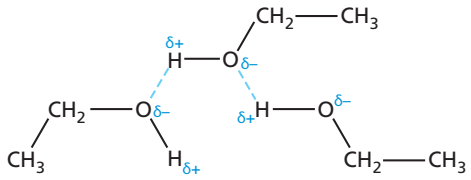
7

PROPERTIES

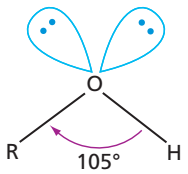
Alcohols have higher boiling points than other organic molecules with similar relative molecular masses.

Methanol, with the lowest molar mass, is a liquid at room temperature.

This is because of hydrogen bonding along with van der Waals' forces between alcohol molecules. This also explains why smaller alcohol molecules mix and dissolve so well in water.



Intermolecular hydrogen bonding in ethanol



The oxygen atom in an alcohol has two lone pairs of electrons

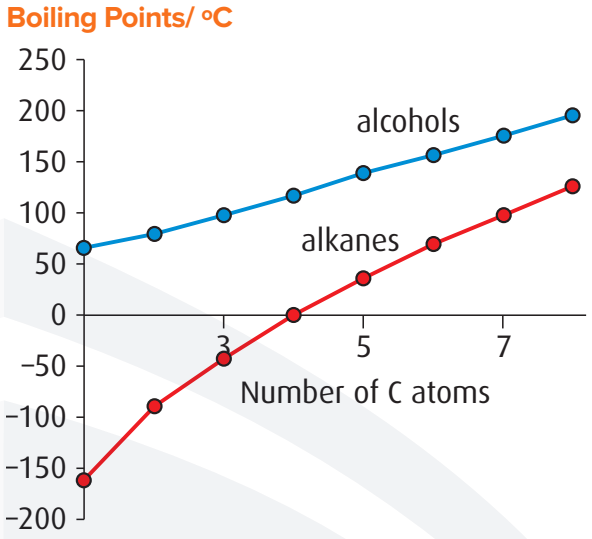
8

BOILING POINTS

The forces between molecules must be broken for the liquid to boil.

In alcohols, hydrogen bonding is the strongest intermolecular force, therefore, more energy is needed to break the hydrogen bonds.

And so the boiling points of alcohols is higher.



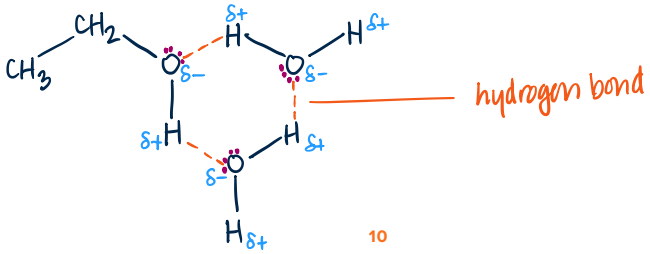
9

SOLUBILITY

The lower members of the series are very soluble in water because of the hydrogen bonding.

For example, ethanol is soluble in water in all proportions, and this is because the –OH group allows it to hydrogen bond to water.

However, solubility decreases as the length of the hydrocarbon chain increases so that pentan-1-ol and hexan-1-ol are only sparingly soluble in water.



10

COMBUSTION OF ALCOHOLS

In a plentiful supply of oxygen, alcohols burn to produce carbon dioxide and water:

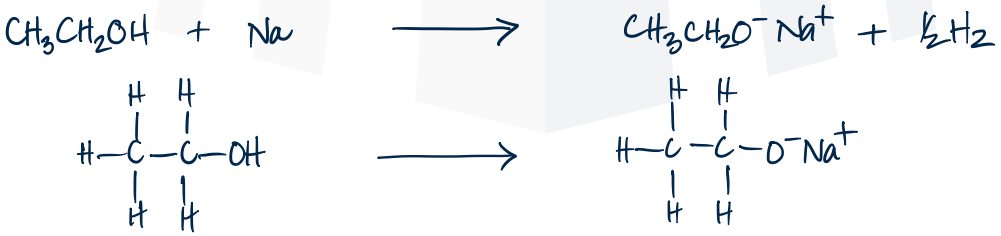
$$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$$

$$2\,C_3H_7OH + 9O_2 \longrightarrow 6CO_2 + 8H_2O$$

11

REACTION WITH SODIUM

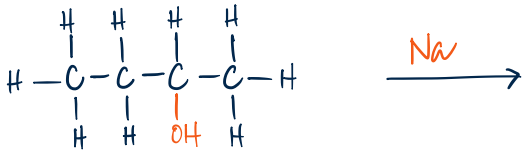
Reagent Sodium metal, Na
Condition room temperature



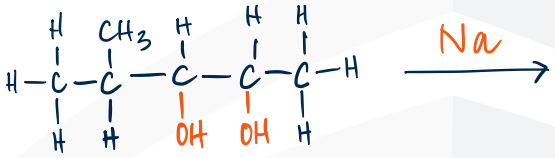
Alcohols are organic chemistry's equivalent of water; water reacts with sodium to produce hydrogen and so do alcohols. The reaction is slower with alcohols.

12

REACTION WITH SODIUM



$CH_3CH_2CH(OH)CH_3$



$(CH_3)_2CHCH(OH)CH(OH)CH_3$

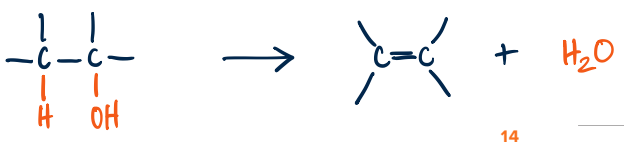
13

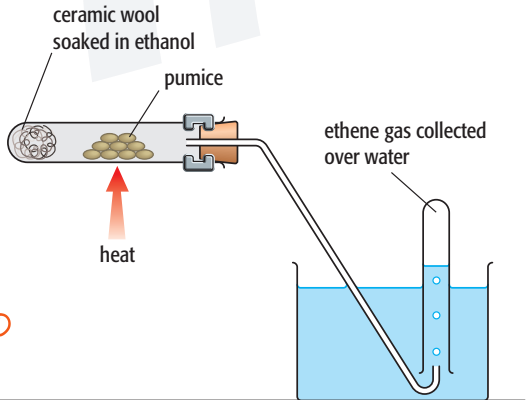
ALCOHOLS TO ALKENES

When an alcohol is heated with excess concentrated sulphuric acid at around 200 °C an alkene is formed. (Refer to the notes on Alkenes).

Dehydration of the alcohol can also be carried out by passing the alcohol vapour over alumina at 350 °C.

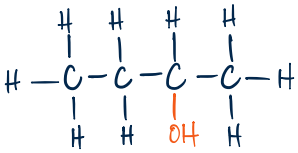
Reagent conc H_2SO_4
Condition 200 °C
Alternatively Alumina at 350°C.
Type Elimination





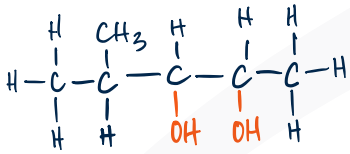
14

ALCOHOLS TO ALKENES



conc. H_2SO_4 and heat →

$CH_3CH_2CH(OH)CH_3$



Al_2O_3 and heat →

$(CH_3)_2CHCH(OH)CH(OH)CH_3$

15

ALCOHOLS TO HALOGENOALKANES

Reagent PCl_5, (PCl_3 or $SOCl_2$)

Condition room temperature (heat for PCl_3 and $SOCl_2$)

Type nucleophilic substitution

The reaction releases white fumes of HCl with PCl_5

NOTE: This is another test for the "OH" group in alcohols and carboxylic acids

16

ALCOHOLS TO HALOGENOALKANES

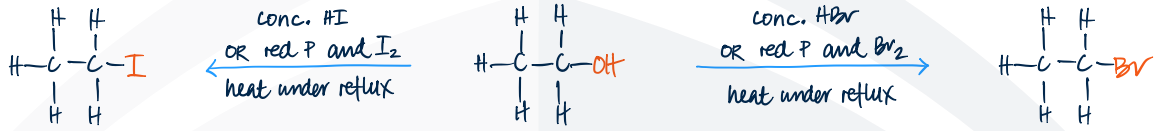
Reagent conc. HBr or conc. HI

Condition heat under reflux

Type nucleophilic substitution

Alternatively Red Phosphorous and Br_2 or Red Phosphorous and I_2 can also be used.

Conc H_2SO_4 and NaBr can also be used to produce conc HBr.



17

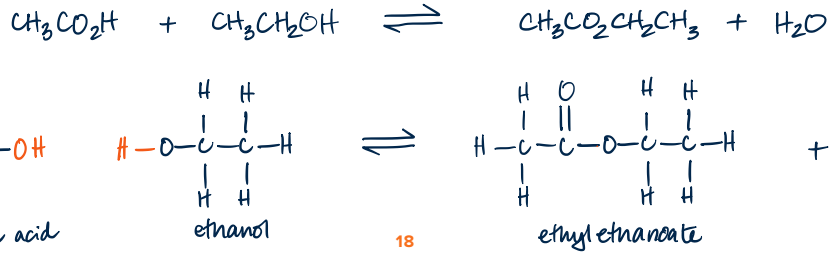
ALCOHOL TO ESTERS

When an alcohol is heated with a carboxylic acid in the presence of a small amount of concentrated sulfuric acid as a catalyst, an ester is formed.

Reagent carboxylic acid and conc. sulfuric acid, H_2SO_4

Condition 60°C / heat

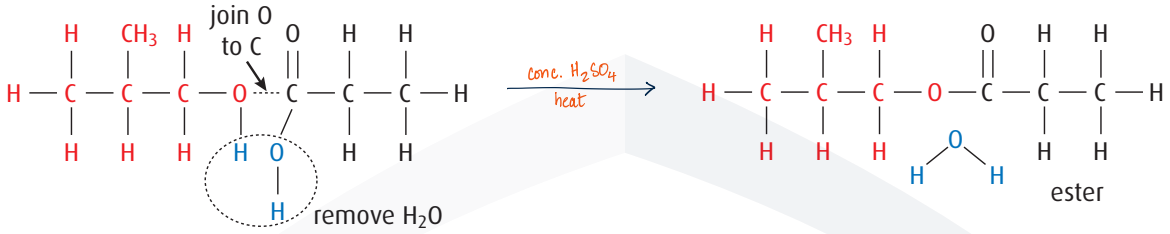
Type esterification / condensation / nucleophilic substitution



18

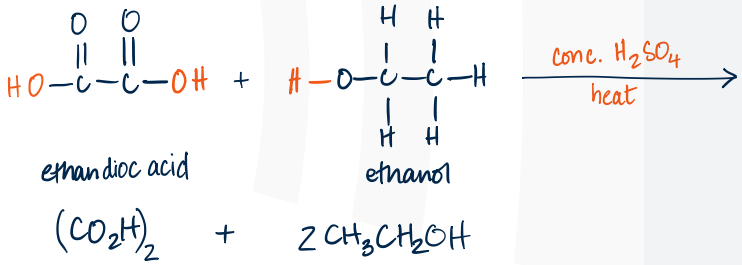
ALCOHOL TO ESTERS

The alcohol and the carboxylic acid have been joined together and water has been eliminated (one H atom from the alcohol and –OH from the carboxylic acid molecule).

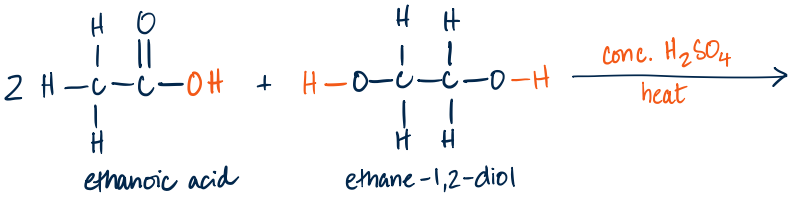


19

ALCOHOL TO ESTERS



$(CO_2H)_2$ + $2\,CH_3CH_2OH$



20

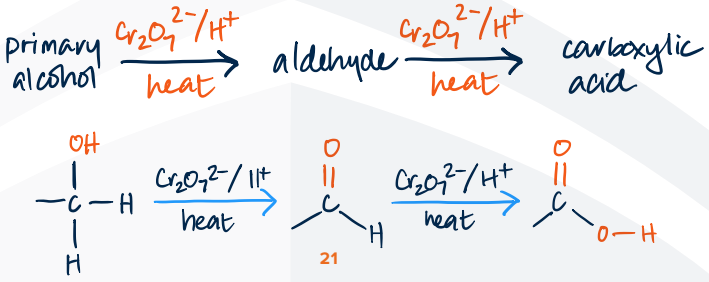
OXIDATION

Primary and secondary alcohols may be oxidised using an oxidising agent, such as:

acidified potassium dichromate(VI) ($K_2Cr_2O_7/H^+$), or

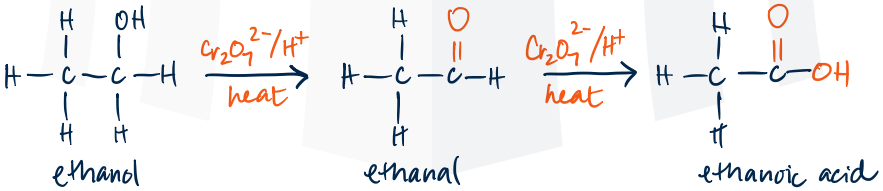
acidified potassium manganate(VII) ($KMnO_4/H^+$).

Primary alcohols are oxidised first of all to an aldehyde (partial oxidation), and then the aldehyde is oxidised further to a carboxylic acid (complete oxidation).



OXIDATION OF PRIMARY ALCOHOLS

Primary alcohols are oxidised to aldehydes, which, in turn, are even more easily oxidised to carboxylic acids. For example:

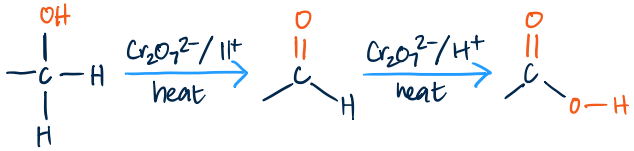


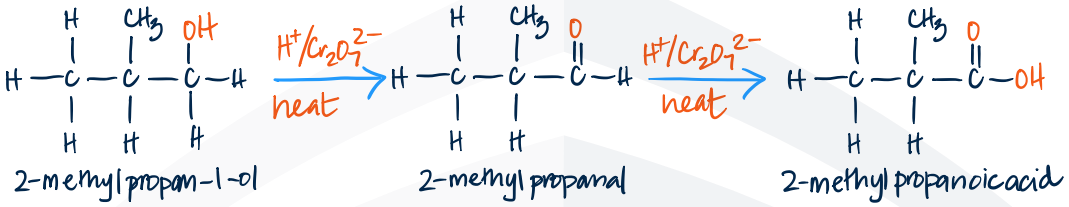
$$CH_3CH_2OH + [O] \longrightarrow CH_3CHO + H_2O$$

$$CH_3CHO + [O] \longrightarrow CH_3CO_2H$$

22

OXIDATION OF PRIMARY ALCOHOLS





23

OXIDATION OF PRIMARY ALCOHOLS

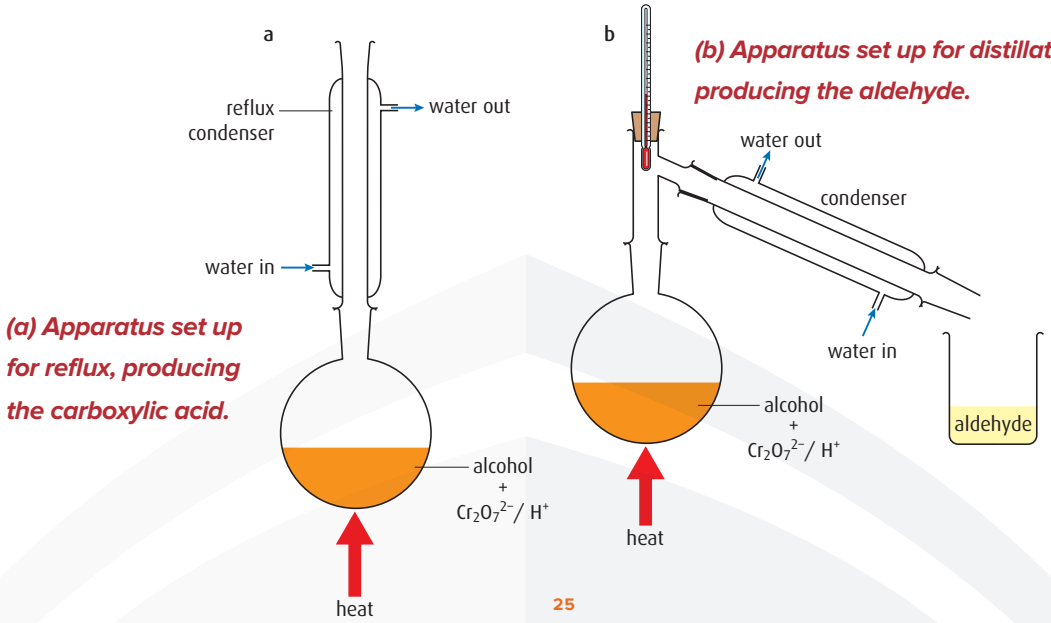
As soon as any aldehyde is formed it can be oxidised further by the oxidising agent, to the carboxylic acid, and so special techniques are needed to stop the oxidation at the aldehyde stage.

One such method makes use of the lower volatility of the alcohol (due to hydrogen bonding) compared with the aldehyde. The reaction mixture is warmed to a temperature that is above the boiling point of the aldehyde, but below that of the alcohol.

The aldehyde is allowed to distill out as soon as it is formed, thus avoiding any further contact with the oxidising agent.

24

OXIDATION OF PRIMARY ALCOHOLS

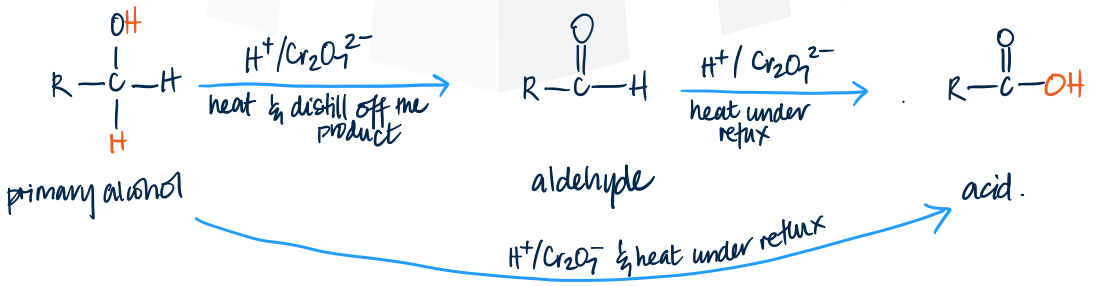


25

OXIDATION OF PRIMARY ALCOHOLS

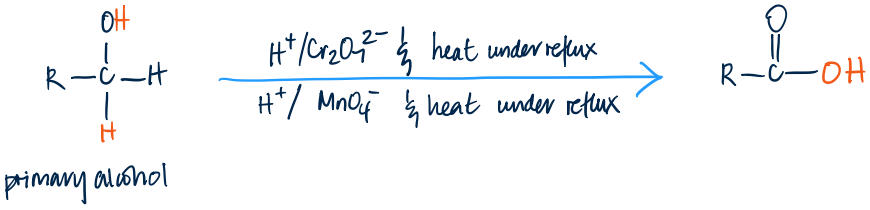
If the reaction mixture is heated under reflux, carboxylic acid is obtained as the main product and the aldehyde is not usually isolated.

However, it is possible to set up the experiment so that the aldehyde is distilled off as soon as it is formed and before it can be oxidised further.



26

OXIDATION OF PRIMARY ALCOHOLS



Using an excess of oxidising agent and heating the reaction under reflux to prevent any escape of the aldehyde before distillation, allows the alcohol to be oxidised all the way to the carboxylic acid.

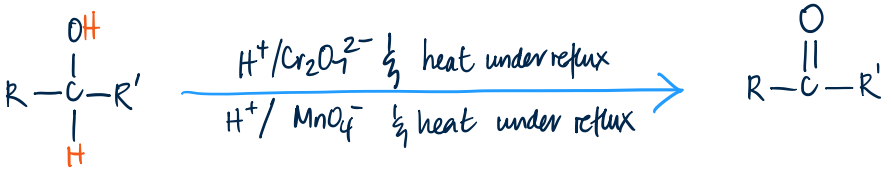
This oxidation reaction can be used to distinguish between primary, secondary and tertiary alcohols.

27

OXIDATION OF SECONDARY ALCOHOLS

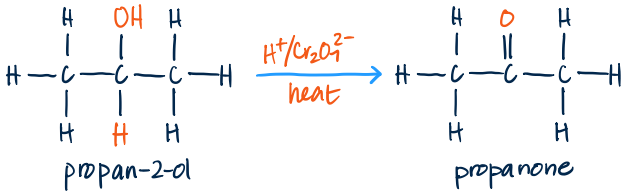
Secondary alcohols are also oxidised by heating with acidified potassium dichromate(VI) (or acidi ed potassium manganate(VII)).

They are oxidised to ketones, which cannot be oxidised any further.

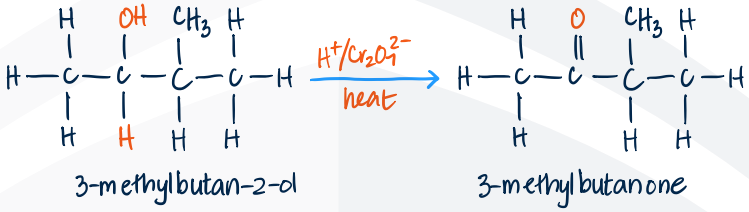


28

OXIDATION OF SECONDARY ALCOHOLS



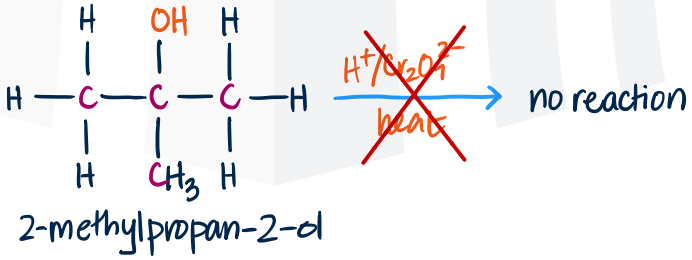
$CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$



29

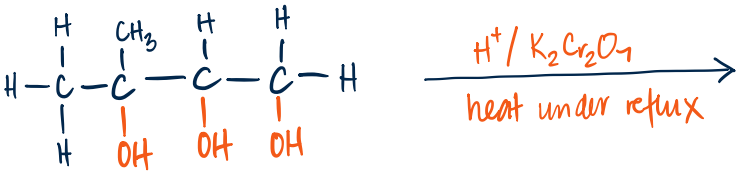
OXIDATION OF TERTIARY ALCOHOLS

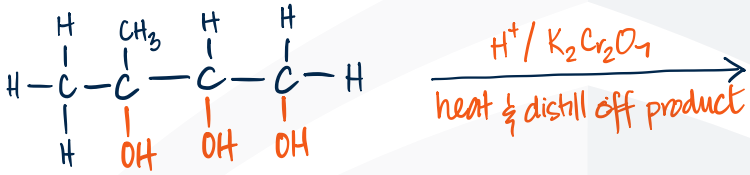
Tertiary alcohols are resistant to oxidation.



30

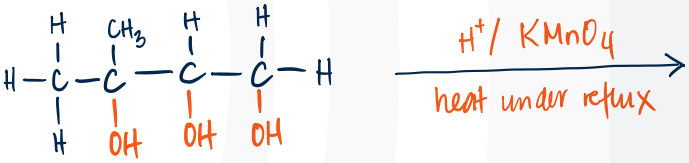
OXIDATION EXAMPLES

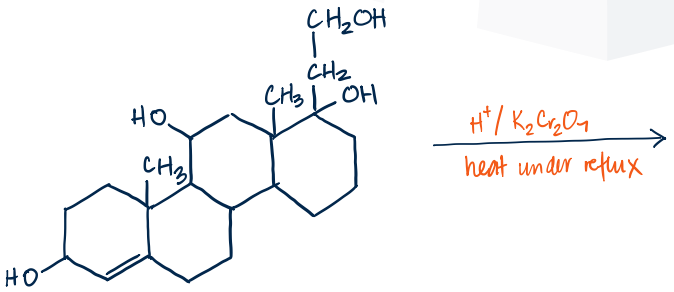




31

OXIDATION EXAMPLES

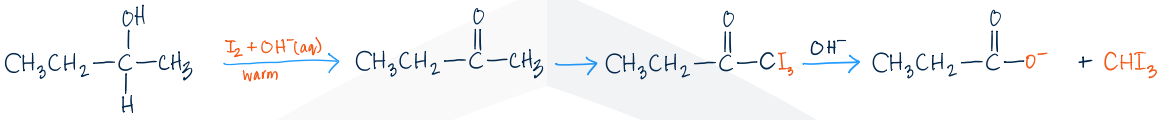




32

IODOFORM REACTION

Alcohols that contain the group $CH_3CH(OH)$-, that is, those that have a methyl group and a hydrogen atom on the same carbon atom that bears the OH group, can be oxidised by alkaline aqueous iodine to the corresponding carbonyl compound $CH_3C(O)$-, which is further oxidised a salt of a carboxylic acid (with one less carbon) and a pale yellow ppt of tri-iodomethane.

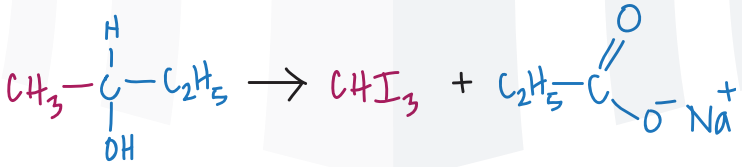


The overall reaction is:

33

IODOFORM REACTION

Except for ethanol, all the alcohols that undergo this reaction are secondary alcohols, with the OH group on the second carbon atom of the chain, that is, they are alkan-2-ols.



34

IODOFORM REACTION

The exception, ethanol, is the only primary alcohol to give the pale yellow precipitate of tri-iodomethane (iodoform) with alkaline aqueous iodine:

35

IODOFORM REACTION

Which of these alcohols will undergo the iodoform reaction?

36

TESTS FOR THE PRESENCE OF 'OH' GROUP

1. With phosphorous pentachloride, PCl_5, gives white fumes (of HCl)

$$CH_3CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + POCl_3 + HCl$$

2. With sodium, gives out bubbles of gas that gives a pop sound with a lighted splinter (hydrogen).

$$CH_3CH_2OH + Na \longrightarrow CH_3CH_2ONa + \tfrac{1}{2} H_2$$

37

TESTS TO DIFFERENTIATE BETWEEN ALCOHOLS

Warm the alcohol with acidified sodium dichromate. If the orange color of dichromate turns green, distill off the product and then warm it with Fehling's solution.

Tertiary alcohol: The orange color remains unaffected.

Secondary alcohol: The orange color turns green but Fehling's solution is unaffected.

Primary alcohol: The orange color turns green and with Fehling's gives a brick-red precipitate.

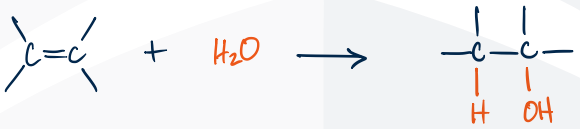
Note: Tollen's reagent can also be used instead of Fehling's solution. The result would be a silver mirror or silver ppt.

38

ALCOHOLS FROM ALKENES

Alkenes react with acid catalyst and steam at temperatures of around 350°C and pressures over 100 atm to form alcohols.

Reagent Steam and dil phosphoric acid (H_3PO_4)
Condition 350 °C and 100 atm
Type Electrophilic addition

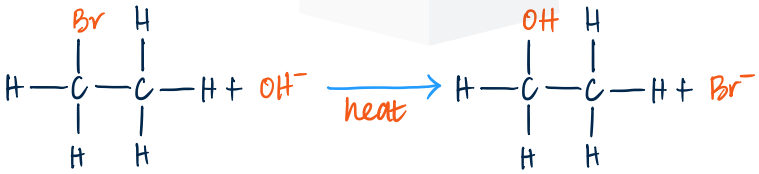


39

ALCOHOLS FROM HALOGENOALKANES

Hydrolysis of halogenoalkanes via NaOH (aq) produces alcohols.

Reagent **Aqueous** sodium (or potassium) hydroxide.
Condition heat under reflux in **aqueous** solution
Type nucleophilic substitution

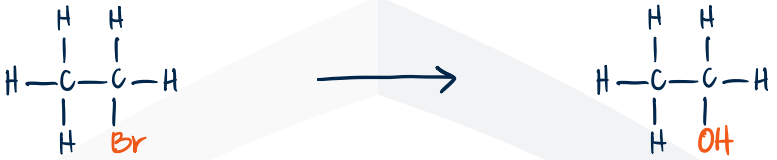


40

ALCOHOLS FROM HALOGENOALKANES

$CH_3CH_2Br + NaOH \longrightarrow CH_3CH_2OH + NaBr$

$CH_3CH_2Br + OH^- \longrightarrow CH_3CH_2OH + Br^-$



41

ALCOHOLS FROM CARBONYLS

Reagent sodium borohydride, $NaBH_4(aq)$ or lithium aluminiumhydride, $LiAlH_4$, in ether.

Condition heat

Type Reduction

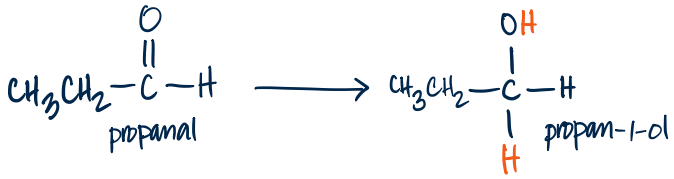
Alternate hydrogen gas over a nickel or platinum catalyst and heat

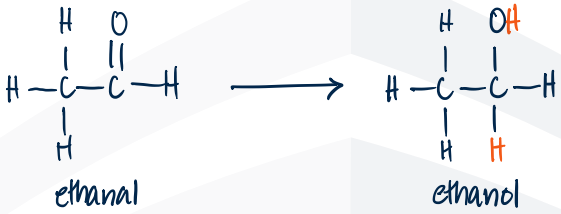
Aldehydes give primary alcohols, while ketones give secondary alcohols.

$RCHO + 2[H] \longrightarrow RCH_2OH$ $\qquad$ $RCOR' + 2[H] \longrightarrow RCH(OH)R'$

42

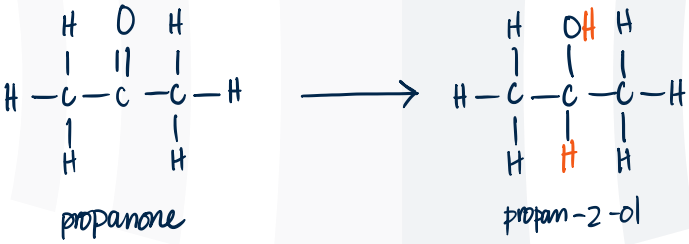
PRIMARY ALCOHOLS FROM ALDEHYDES

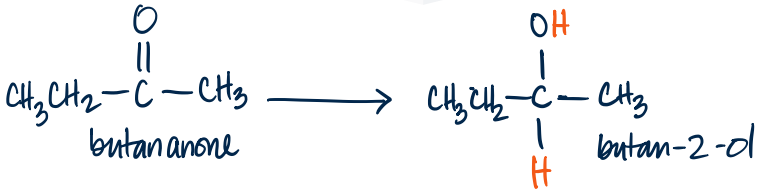




43

SECONDARY ALCOHOLS FROM KETONES





44