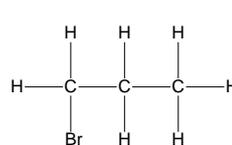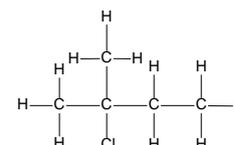# 10 Halogenoalkanes

Naming Halogenoalkanes

Based on original alkane, with a *prefix* indicating halogen atom:
Fluoro for **F**; **Chloro** for **Cl**; **Bromo** for **Br**; **Iodo** for **I**.
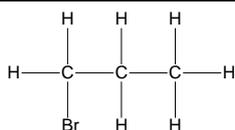
Substituents are listed **alphabetically**
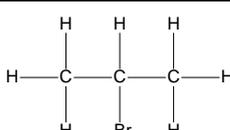
1-bromopropane   2-chloro-2-methylbutane

Classifying Halogenoalkanes

Halogenoalkanes can be classified as primary, secondary or tertiary depending on the number of carbon atoms attached to the C-X functional group.
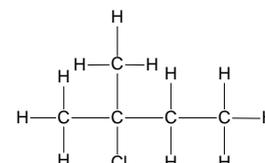
Primary halogenoalkane
One carbon attached to the carbon atom adjoining the halogen

Secondary halogenoalkane
Two carbons attached to the carbon atom adjoining the halogen

Tertiary halogenoalkane
Three carbons attached to the carbon atom adjoining the halogen

Reactions of Halogenoalkanes

Halogenoalkanes undergo either **substitution** or **elimination** reactions

Nucleophilic substitution reactions

Substitution: swapping a halogen atom for another atom or groups of atoms

Nucleophile: electron pair donor e.g. :OH$^-$, :NH$_3$, CN$^-$

The mechanism: We draw (or **outline**) mechanisms to show in detail how a reaction proceeds

:Nu represents any nucleophile – they always have a **lone pair** and act as **electron pair donors**

The nucleophiles attack the positive carbon atom
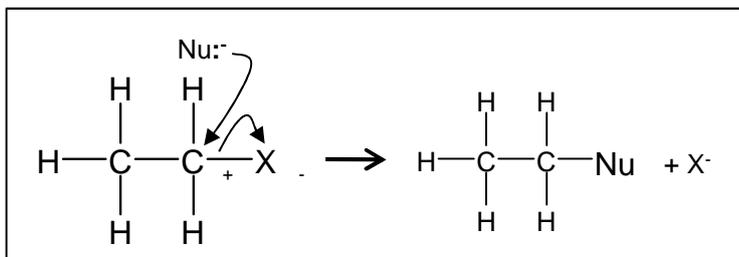
The carbon has a small positive charge because of the electronegativity difference between the carbon and the halogen

We use curly arrows in mechanisms (with two line heads) to show the movement of two electrons

A curly arrow will always **start** from a **lone pair** of electrons or the **centre of a bond**

The rate of these substitution reactions depends on the strength of the C-X bond
The weaker the bond, the easier it is to break and the faster the reaction.

The iodoalkanes are the fastest to substitute and the fluoroalkanes are the slowest. The strength of the C-F bond is such that fluoroalkanes are very unreactive

	Bond enthalpy / kJmol^{-1}
C-I	238
C-Br	276
C-Cl	338
C-F	484

Comparing the rate of hydrolysis reactions

Hydrolysis is defined as the splitting of a molecule (in this case a halogenoalkane) by a reaction with water

$$CH_3CH_2X + H_2O \rightarrow CH_3CH_2OH + X^- + H^+$$

Aqueous silver nitrate is added to a halogenoalkane and the halide leaving group combines with a silver ion to form a **silver halide precipitate**.
The precipitate only forms when the halide ion has left the halogenoalkane and so the rate of formation of the precipitate can be used to compare the reactivity of the different halogenoalkanes.

The **quicker** the **precipitate** is formed, the **faster** the **substitution** reaction and the **more reactive** the haloalkane

The rate of these substitution reactions depends on the strength of the C-X bond . The weaker the bond, the easier it is to break and the faster the reaction.

If the experiment is repeated using primary, secondary and tertiary halogenoalkanes, the order of reactivity will be:
Tertiary   >   secondary > primary
Reacts first

Water is a *poor* **nucleophile** but it can react **slowly** with halogenoalkanes in a substitution reaction

$$CH_3CH_2I + H_2O \rightarrow CH_3CH_2OH + I^- + H^+$$

$$Ag^+_{(aq)} + I^-_{(aq)} \rightarrow AgI_{(s)} \text{ - yellow precipitate}$$

The iodoalkane forms a precipitate with the silver nitrate first as the C-I bond is weakest and so it hydrolyses the quickest

$AgI_{(s)}$ - yellow precipitate
$AgBr_{(s)}$ – cream precipitate
$AgCl_{(s)}$ – white precipitate   ↑ forms faster

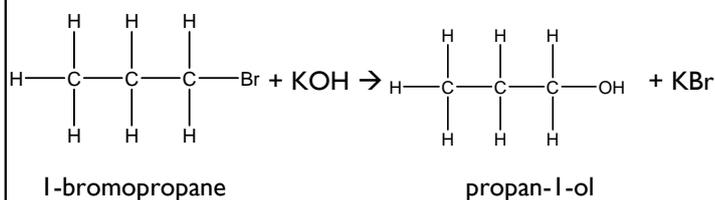## Nucleophilic substitution with <u>aqueous</u> hydroxide ions

Change in functional group: halogenoalkane → alcohol
Reagent: potassium (or sodium) hydroxide
Conditions: In **aqueous solution**; Heat under reflux
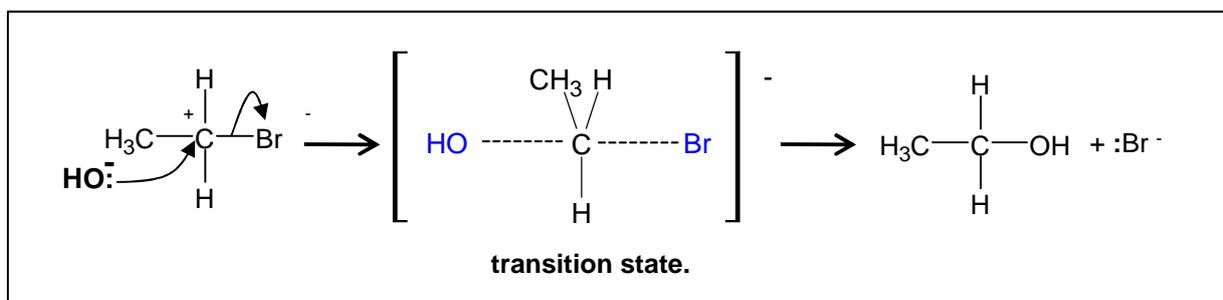**Mechanism**: Nucleophilic substitution
Role of reagent: Nucleophile, OH⁻

1-bromopropane   propan-1-ol

The OH⁻ is a stronger nucleophile than water as it has a full negative charge and so is more strongly attracted to the C $^+$

The **aqueous** conditions needed is an important point. If the solvent is changed to **ethanol** an elimination reaction occurs

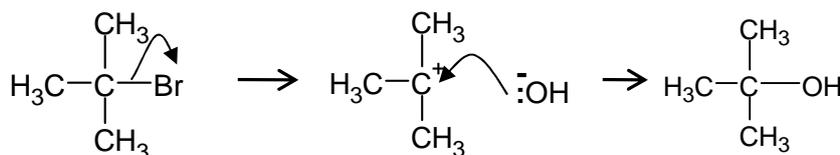### SN$_2$ nucleophilic substitution mechanism for halogenoalkanes

transition state.

This mechanism occurs with primary halogenoalkanes

SN₁ nucleophilic substitution mechanism for tertiary halogenoalkanes

Tertiary haloalkanes undergo nucleophilic substitution in a different way

The Br first breaks away from the haloalkane to form a carbocation intermediate

The hydroxide nucleophile then attacks the positive carbon

Tertiary halogenoalkanes undergo this mechanism as the tertiary carbocation is stabilised by the electron releasing methyl groups around it. (see alkenes topic for another example of this). Also the bulky methyl groups prevent the hydroxide ion from attacking the halogenoalkane in the same way as the mechanism above.

Primary halogenoalkanes do not do the SN₁ mechanism because they would only form an unstable primary carbocation.
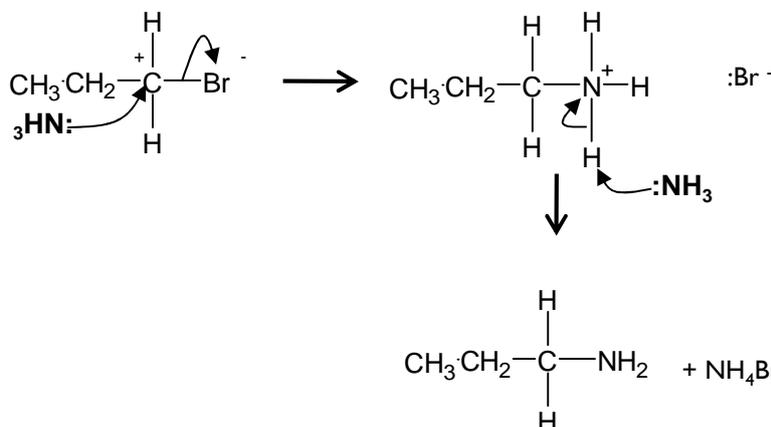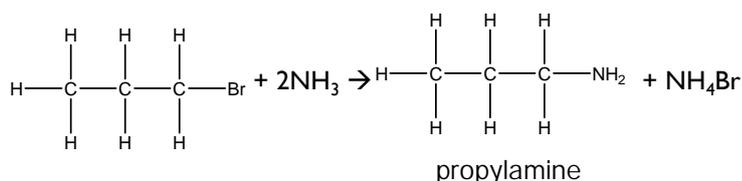
Nucleophilic substitution with ammonia

Change in functional group: halogenoalkane → amine

Reagent: NH_3 dissolved in ethanol

Conditions: Heating under pressure in a sealed tube

Mechanism: Nucleophilic substitution

**Type of reagent**: Nucleophile, :NH_3

propylamine

Naming amines:

In the above example prop**yl**amine, the propyl shows the 3 C's of the carbon chain.

Sometimes it is easier to use the IUPAC naming for amines e.g. Prop**an-1-amine**

Further substitution reactions can occur between the halogenoalkane and the amines formed leading to a lower yield of the amine. Using excess ammonia helps minimise this.

Further reactions
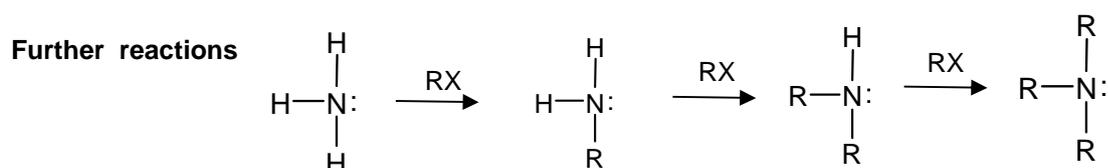
Elimination reaction of halogenoalkanes

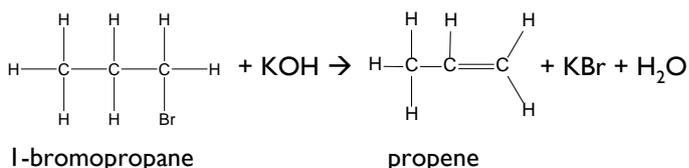## Elimination with alcoholic hydroxide ions

Change in functional group: halogenoalkane →
alkene
Reagents: Potassium (or sodium) hydroxide
Conditions: In **ethanol** ; Heat
Mechanism: Elimination
Role of reagent: Base, OH⁻

1-bromopropane + KOH → propene + KBr + H_2O

Note the importance of the solvent to the type of reaction here.

Aqueous: substitution

Alcoholic: elimination

Often a mixture of products from both elimination and substitution occurs

With unsymmetrical secondary and tertiary halogenoalkanes two (or sometimes three) different structural isomers can be formed

2-methyl -2-chlorobutane can give 2-methylbut-1-ene and 2-methylbut-2-ene
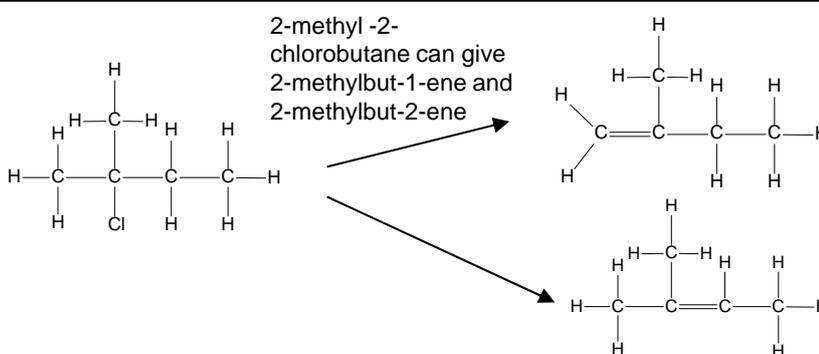
The structure of the halogenoalkane also has an effect on the degree to which substitution or elimination occurs in this reaction.

Primary tends towards substitution

Tertiary tends towards elimination

Uses of halogenoalkanes

Haloalkanes have been used as **refrigerants, fire retardants,** pesticides and **aerosol propellants**

Chloroalkanes and chlorofluoroalkanes can be used as solvents.

CH_3CCl_3 was used as the solvent in dry cleaning

Some halogenoalkanes have low flammability

Many of these uses have now been stopped due to the toxicity of halogenoalkanes and also their detrimental effect on the ozone layer.
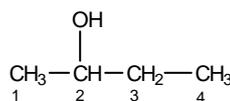
6E Alcohols

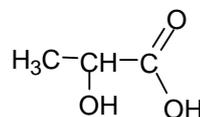General formula alcohols $C_nH_{2n+1}OH$

Naming Alcohols

These have the ending **-ol** and if necessary the position number for the OH group is added between the name stem and the –ol

Butan-2-ol

If the compound has an –OH group in addition to other functional groups that need a suffix ending then the OH can be named with the prefix **hydroxy-**):
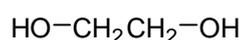
2-hydroxypropanoic acid

$HO-CH_2CH_2-OH$ Ethan**e**-1,2-diol

If there are two or more -OH groups then di, tri are used.
Add the **'e'** on to the stem name though
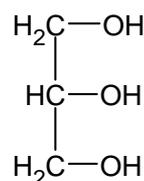
propan**e**-1,2,3-triol
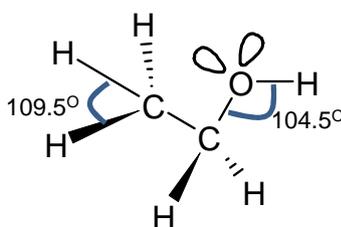
Bond angles in alcohols

All the H-C-H bonds and C-C-O are 109.5° (tetrahedral shape), because there are 4 bond pairs of electrons repelling to a position of minimum repulsion.

109.5°   104.5°

The H-O- C bond is 104.5° (bent line shape), because there are 2 bond pairs of electrons and 2 lone pairs repelling to a position of minimum repulsion. Lone pairs repel more than bond pairs so the bond angle is reduced.

Different types of alcohols
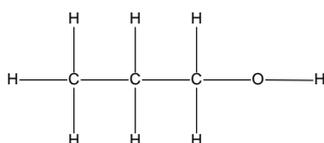
propan-1-ol
Primary

propan-2-ol
Secondary

methylpropan-2-ol
Tertiary

Primary alcohols are alcohols where 1 carbon is attached to the carbon adjoining the oxygen

Secondary alcohols are alcohols where 2 carbon are attached to the carbon adjoining the oxygen

Tertiary alcohols are alcohols where 3 carbon are attached to the carbon adjoining the oxygen

1. Combustion of Alcohols

Alcohols combust with a clean flame
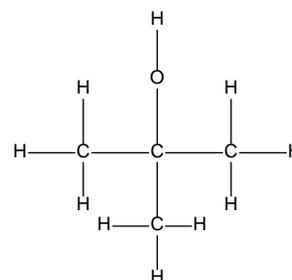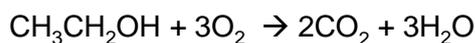
$$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

2. Substitution reactions of Alcohols to form Halogenoalkanes

Various halogenating compounds can be used to substitute the –OH group for a halogen

PCl_5 / PCl_3 / conc HCl / $SOCl_2$ / mixture of NaCl + H_2SO_4 can all be uses for substituting a Cl

Reaction with phosphorous (V) halide

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

This reaction with PCl_5 (phosphorous(V)chloride) can be used as a test for alcohols. You would observe misty fumes of HCl produced.

$$CH_3CH_2OH + HBr \rightarrow CH_3CH_2Br + H_2O$$
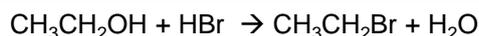
For Br use KBr, 50% concentrated H_2SO_4 to produce HBr

Reaction with phosphorous (III) iodide

$$PI_3 + 3\ CH_3CH_2OH \rightarrow 3CH_3CH_2I + H_3PO_3$$

The **phosphorous (III) Iodide** is produced in situ by reacting red phosphorus and Iodine.

The reaction of KI and conc H_2SO_4 can't be used to produce HI because the sulfuric acid will oxidise the hydrogen halides to other products.

3. Oxidation reactions of the alcohols

Potassium dichromate $K_2Cr_2O_7$ is an oxidising agent that causes alcohols to oxidise.

The exact reaction, however, depends on the type of alcohol, i.e. whether it is primary, secondary, or tertiary, and on the conditions.

Partial Oxidation of Primary Alcohols

Reaction: primary alcohol → aldehyde
Reagent: potassium dichromate (VI) solution and dilute sulfuric acid.
Conditions: (use a limited amount of dichromate) warm gently and **distil** out the aldehyde as it forms:

Ethan**al**
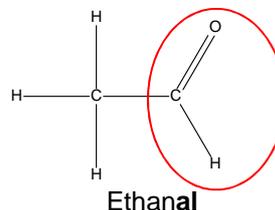
An aldehyde's name ends in **–al**
It always has the C=O bond on the first carbon of the chain so it does not need an extra number

Observation: the orange dichromate ion ($Cr_2O_7{}^{2-}$) reduces to the green Cr $^{3+}$ ion

$$CH_3CH_2CH_2OH + [O] \rightarrow CH_3CH_2CHO + H_2O$$
propan-1-ol   **propanal**

Write the oxidation equations in a simplified form using [O] which represents O from the oxidising agent

When writing the formulae of aldehydes in a condensed way write **CHO** and not COH e.g.CH_3CH_2**CHO**
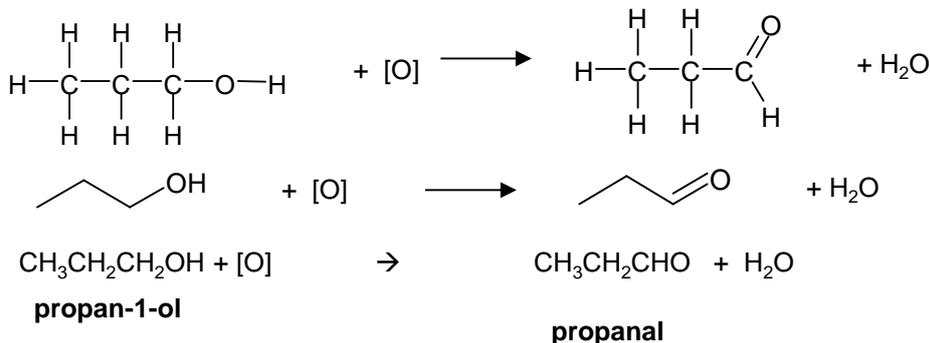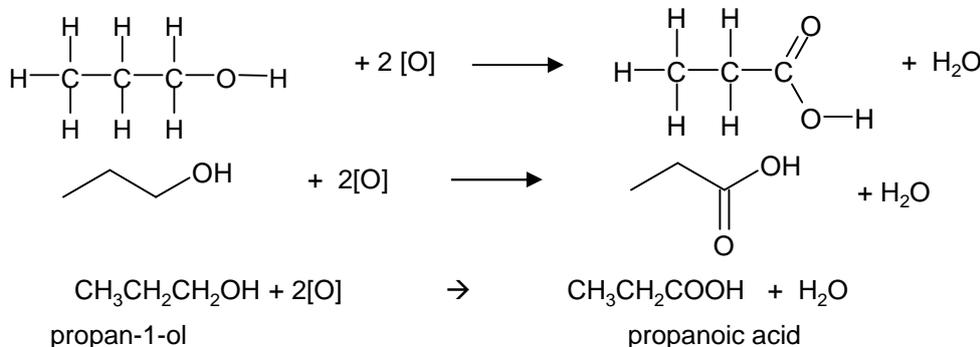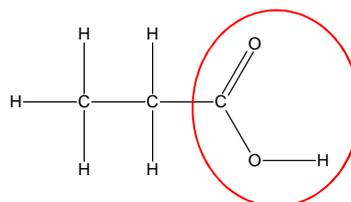
Full Oxidation of Primary Alcohols

Reaction: primary alcohol → carboxylic acid

Reagent: potassium dichromate(VI) solution and dilute sulfuric acid

Conditions: use an excess of dichromate, and **heat under reflux**: (distil off product after the reaction has finished)
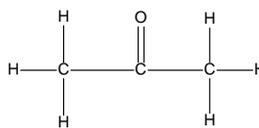

Propanoic acid

Observation: the orange dichromate ion ($Cr_2O_7^{2-}$) reduces to the green Cr^{3+} ion

$$CH_3CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2COOH + H_2O$$

propan-1-ol   propanoic acid

Oxidation of Secondary Alcohols

Reaction: secondary alcohol → ketone
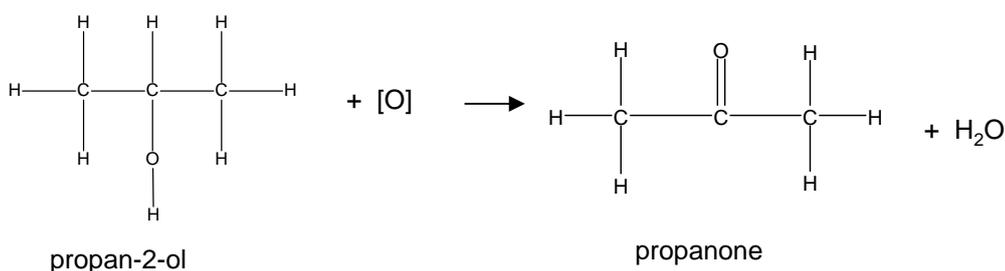
Reagent: potassium dichromate(VI) solution and dilute sulfuric acid.

Conditions: heat under reflux

propan**one**

Ketones end in **-one**

When ketones have 5C's or more in a chain then it needs a number to show the position of the double bond. E.g. pentan-2-one

propan-2-ol   propanone

Observation: the orange dichromate ion ($Cr_2O_7^{2-}$) reduces to the green Cr^{3+} ion

There is no further oxidation of the ketone under these conditions.

Tertiary alcohols cannot be oxidised at all by potassium dichromate: This is because there is no hydrogen atom bonded to the carbon with the OH group

Distinguishing between Aldehydes and Ketones

The fact that aldehydes can be further oxidised to carboxylic acids whereas ketones cannot be further oxidised is the chemical basis for tests that are commonly used to distinguish between aldehydes and ketones

Fehling's (Benedict's) solution

Reagent: Fehling's Solution containing blue Cu^{2+} ions.

Conditions: heat gently

Reaction: aldehydes only are oxidised by Fehling's solution into a carboxylic acid. The copper (II) ions are reduced to copper(I) oxide

Observation: Aldehydes :Blue Cu^{2+} ions in solution change to a red precipitate of Cu_2O. **Ketones do not react**

$$CH_3CHO + 2Cu^{2+} + 2H_2O \rightarrow CH_3COOH + Cu_2O + 4H^+$$
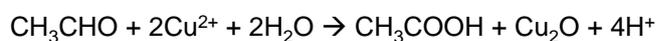
The presence of a carboxylic acid can be tested by addition of sodium carbonate. It will fizz and produce carbon dioxide

Reaction of Alcohols with Dehydrating Agents

Reaction: Alcohol → Alkene

Reagents: Concentrated phosphoric acid
Conditions: warm (under reflux)
Role of reagent: dehydrating agent/catalyst
Type of reaction: **acid catalysed** elimination

Dehydration reaction: removal of a water molecule from a molecule

propan-1-ol → **propene** + H_2O

$$CH_3CH_2CH_2OH \rightarrow CH_2=CHCH_3 + H_2O$$
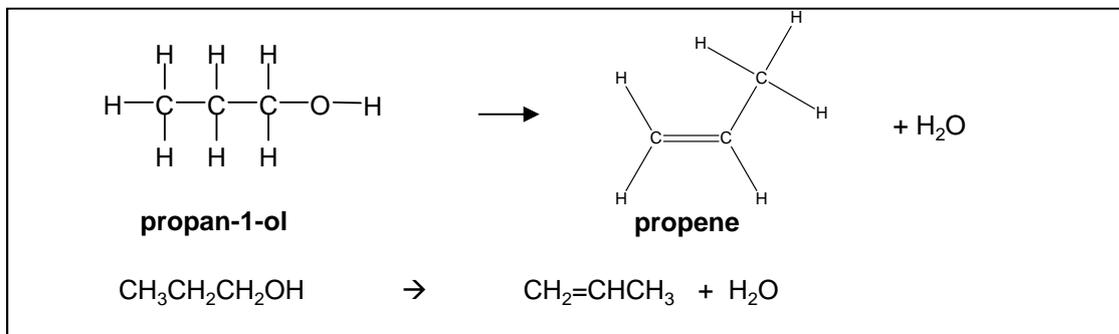
Some 2° and 3° alcohols can give more than one product, when the double bond forms between different carbon atoms

butan-2-ol

but-1-ene

but-2-ene

Butan-2-ol can form both alkenes although more but-2-ene would be formed

But-2-ene could also exist as E and Z isomers
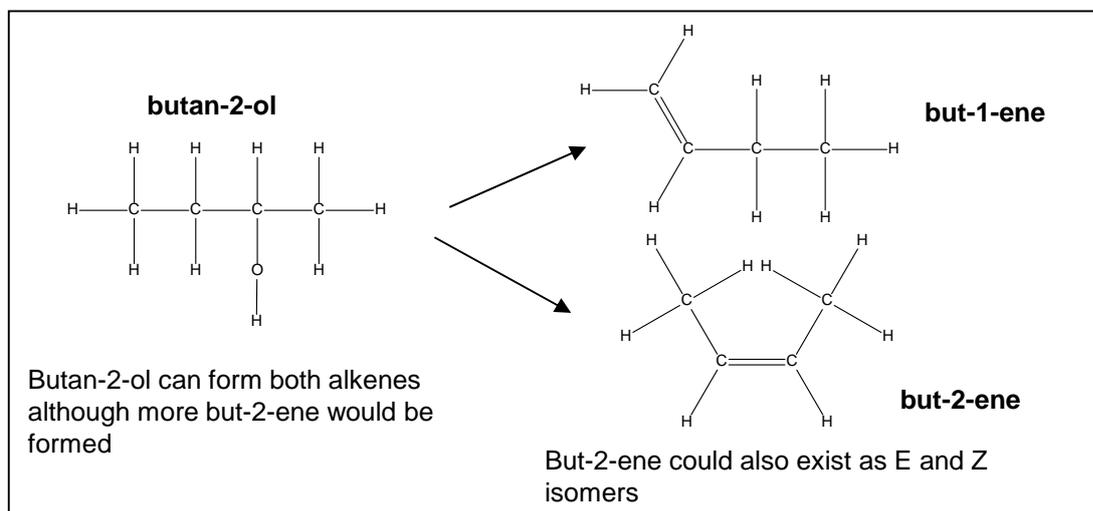
Producing alkenes from alcohols provides a possible route to polymers without using monomers derived from oil

Organic techniques

Distillation

In general used as separation technique to separate an organic product from its reacting mixture. Need to collect the distillate of the approximate boiling point range of the desired liquid.

It's important to be able to draw and label this apparatus accurately. Don't draw lines between flask, adaptor and condenser.
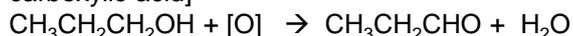
thermometer

Liebig condenser

Water out

Water in

Round bottomed flask

Heat

Classic reaction using distillation
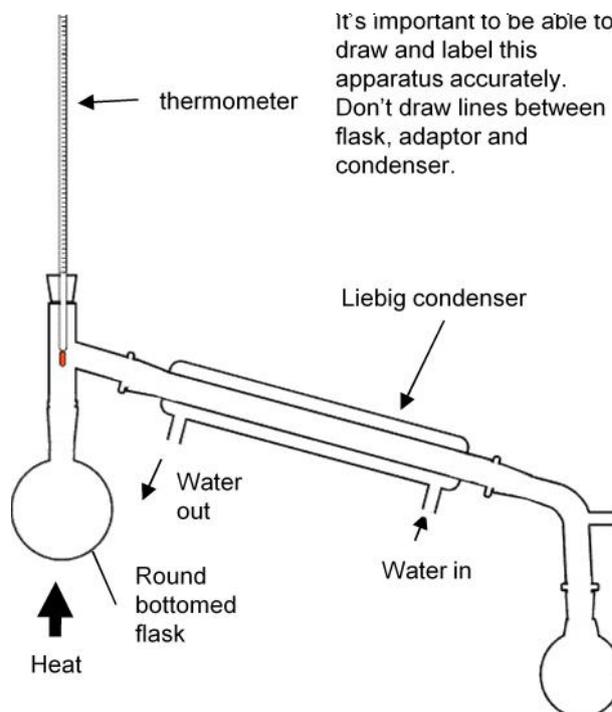**Reaction**: primary alcohol → aldehyde
Reagent: potassium dichromate (VI) solution and dilute sulfuric acid.
Conditions: use a limited amount of dichromate and **warm gently and distil** out the aldehyde as it forms [This prevents further oxidation to the carboxylic acid]
$CH_3CH_2CH_2OH + [O] \rightarrow CH_3CH_2CHO + H_2O$
Observation
Orange dichromate solution changes to green colour of Cr^{3+} ions

Reflux

Reflux is used when heating organic reaction mixtures for long periods. The condenser prevents organic vapours from escaping by condensing them back to liquids.

Water out

condenser

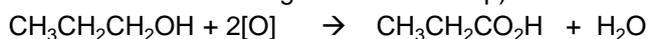Water in

Round bottomed flask

Heat

Never seal the end of the condenser as the build up of gas pressure could cause the apparatus to explode. This is true of any apparatus where volatile liquids are heated

Classic reaction using reflux
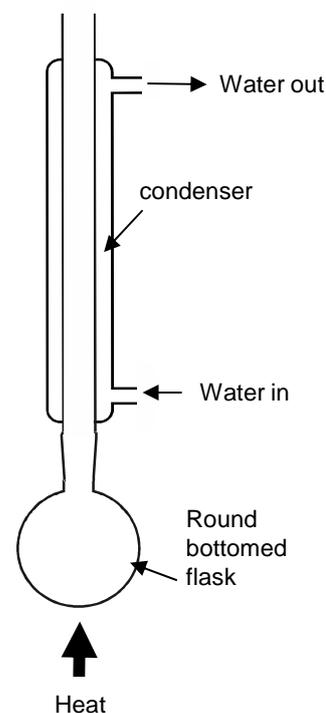**Reaction**: primary alcohol → carboxylic acid
Reagent: potassium dichromate(VI) solution and dilute sulfuric acid
Conditions: use an excess of dichromate, and **heat under reflux**: (distil off product after the reaction has finished using distillation set up)
$CH_3CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2CO_2H + H_2O$
Observation
Orange dichromate solution changes to green colour of Cr^{3+} ions

Anti-bumping granules are added to the flask in both distillation and reflux to prevent vigorous, uneven boiling by **making small bubbles** form instead of large bubbles

It's important to be able to draw and label this apparatus accurately.
- Don't draw lines between flask and condenser.
- Don't have top of condenser sealed
- Condenser must have outer tube for water that is sealed at top and bottom
- Condenser must have two openings for water in and out that are open

Electric heaters are often used to heat organic chemicals. This is because organic chemicals are normally highly flammable and could set on fire with a naked flame.

Purifying an organic liquid

• Put the distillate of impure product into a separating funnel

• wash product by adding either
  • sodium hydrogencarbonate solution , shaking and releasing the pressure from CO_2 produced.
  • Saturated sodium chloride solution

•Allow the layers to separate in the funnel, and then run and discard the aqueous layer.

•Run the organic layer into a clean, dry conical flask and add three spatula loads of drying agent (anhydrous sodium sulfate) to dry the organic liquid.

• Carefully decant the liquid into the distillation flask

•Distil to collect pure product

Sodium hydrogencarbonate will neutralise any remaining reactant acid.

Sodium chloride will help separate the organic layer from the aqueous layer
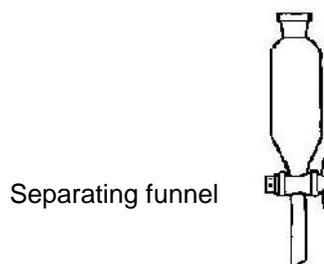
The drying agent should
•be insoluble in the organic liquid
• not react with the organic liquid
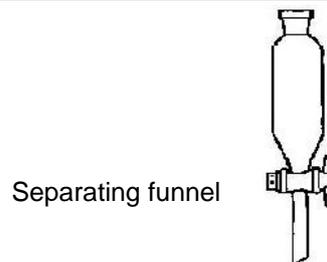
Separating funnel

Solvent extraction

Mix organic solvent and oil-water mixture in a separating funnel then separate the oil layer.
Distil to separate oil from organic solvent
Add anhydrous $CaCl_2$ to clove oil to dry oil
Decant to remove $CaCl_2$

Separating funnel

Measuring boiling point

Purity of liquid can be determined by measuring a boiling point. This can be done in a distillation set up or by simply boiling a tube of the sample in an heating oil bath.

Pressure should be noted as changing pressure can change the boiling point of a liquid

Measuring boiling point is not the most accurate method of identifying a substance as several substances may have the same boiling point.

To get a correct measure of boiling point the thermometer should be above the level of the surface of the boiling liquid and be measuring the temperature of the saturated vapour.

10D. Mass spectra and IR

Mass spectrometry

Measuring the M_r of an organic molecule

If a molecule is put through a mass spectrometer it will often break up and give a series of peaks caused by the fragments. The peak with the largest m/z, however, will be due to the complete molecule and will be equal to the M_r of the molecule. This peak is called the parent ion or **molecular ion**

Spectra for C_4H_{10}

Mass spectrum for butane

43

29

58

Molecular ion $C_4H_{10}^+$
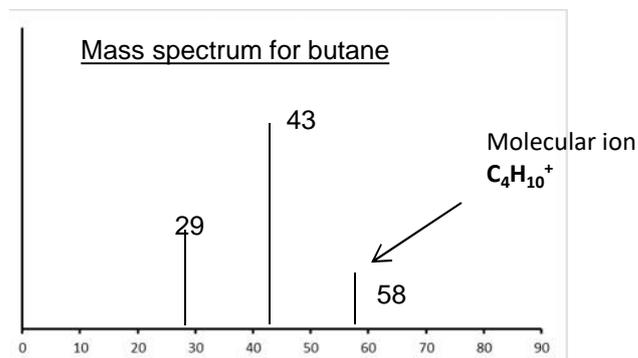
Fragmentation

When organic molecules are passed through a mass spectrometer, it detects both the whole molecule and fragments of the molecule.

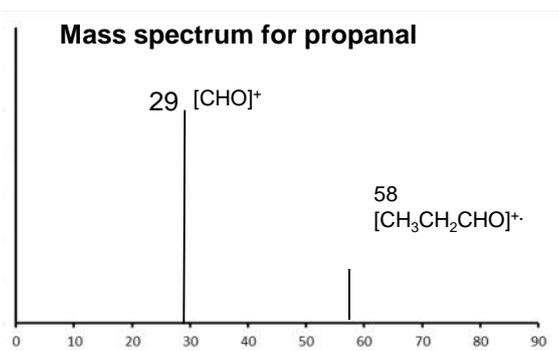Molecular ion formed: M $[M]^{+\cdot} + e^-$

The molecule loses an electron and becomes both an ion and a free radical

Several peaks in the mass spectrum occur due to fragmentation.
The Molecular ion fragments due to covalent bonds breaking: $[M]^{+\cdot}$ $X^+ + Y^\cdot$

This process produces an ion and a free radical. The ion is responsible for the peak

Relatively stable ions such as carbocations R^+ such as $CH_3CH_2^+$ and acylium ions $[R-C=O]^+$ are common. The more stable the ion, the greater the peak intensity.
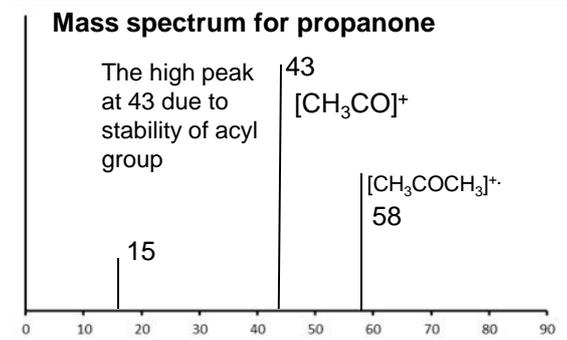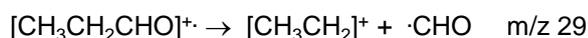
The peak with the highest mass/charge ratio will be normally due to the original molecule that hasn't fragmented (called the molecular ion) . As the charge of the ion is +1 the mass/ charge ratio is equal to Mr.

Mass spectrum for propanal

29 $[CHO]^+$

58 $[CH_3CH_2CHO]^{+\cdot}$

Equation for formation molecular ion

$CH_3CH_2CHO \rightarrow [CH_3CH_2CHO]^{+\cdot} + e^-$ m/z 58

Equations for formation of fragment ions from molecular ions

$[CH_3CH_2CHO]^{+\cdot} \rightarrow [CHO]^+ + \cdot CH_2CH_3$ m/z 29

$[CH_3CH_2CHO]^{+\cdot} \rightarrow [CH_3CH_2]^+ + \cdot CHO$ m/z 29

Mass spectrum for propanone

The high peak at 43 due to stability of acyl group

43 $[CH_3CO]^+$

$[CH_3COCH_3]^{+\cdot}$ 58

15

Equation for formation molecular ion

$CH_3COCH_3 \rightarrow [CH_3COCH_3]^{+\cdot} + e^-$ m/z 58

Equations for formation of fragment ions from molecular ions

$[CH_3COCH_3]^{+\cdot} \rightarrow [CH_3CO]^+ + \cdot CH_3$ m/z 43
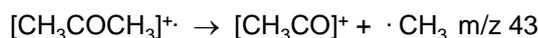
It is not possible for propanone to fragment to give a peak at 29 so the fragmentation patterns can distinguish between the structural isomers of propanone and propanal

Infrared spectroscopy

Certain bonds in a molecule absorb infra-red radiation at characteristic frequencies causing the covalent bonds to vibrate

Complicated spectra can be obtained than provide information about the types of bonds present in a molecule

ABOVE 1500 cm^{-1} – "Functional group identification"
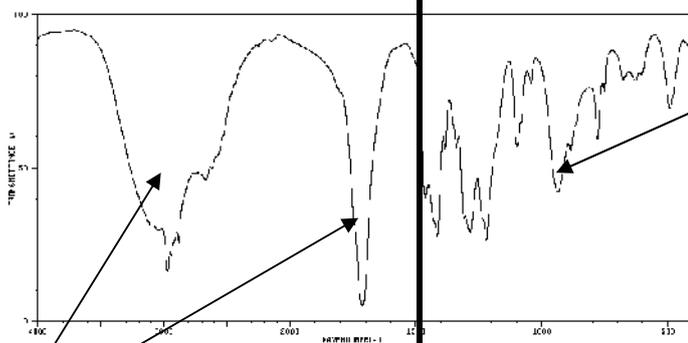
BELOW 1500 cm^{-1} – "Fingerprinting"

Complicated and contains many signals – picking out functional group signals difficult.

This part of the spectrum is unique for every compound, and so can be used as a "fingerprint".
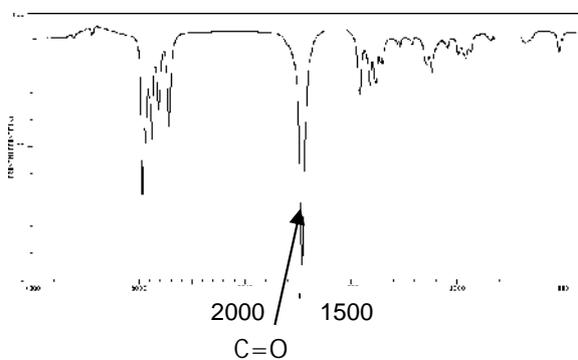
e.g. C=O 1640 – 1750 cm^{-1}

O-H (acid) 2500- 3300 cm^{-1}

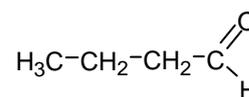A computer will compare the IR spectra against a database of known pure compounds to identify the compound

Use an IR absorption table provided in exam to deduce presence <u>or</u> absence of particular bonds or functional groups

Bond	Wavenumber
C-O	1000-1300
C=O	1640-1750
C-H	2850 -3100
O-H Carboxylic acids	2500-3300 Very broad
N-H	3200-3500
O-H Acohols, phenols	3200- 3550 broad

Use spectra to identify particular functional groups e.g. an alcohol from an absorption peak of the O–H bond, or C=O stretching absorption in aldehydes and ketones


Spectra for butanal

$H_3C-CH_2-CH_2-C$ with O and H

2000 1500

C=O

Absorption or trough in between 1640-1750 cm^{-1} range indicates presence of C=O bond

Spectra for ethanoic acid

O-H absorptions tend to be broad

Absorption or trough in between 2500-3300 cm^{-1} range indicates presence of O-H bond in an acid

C=O

Absorption or trough in between 1640-1750 cm^{-1} range indicates presence of C=O bond
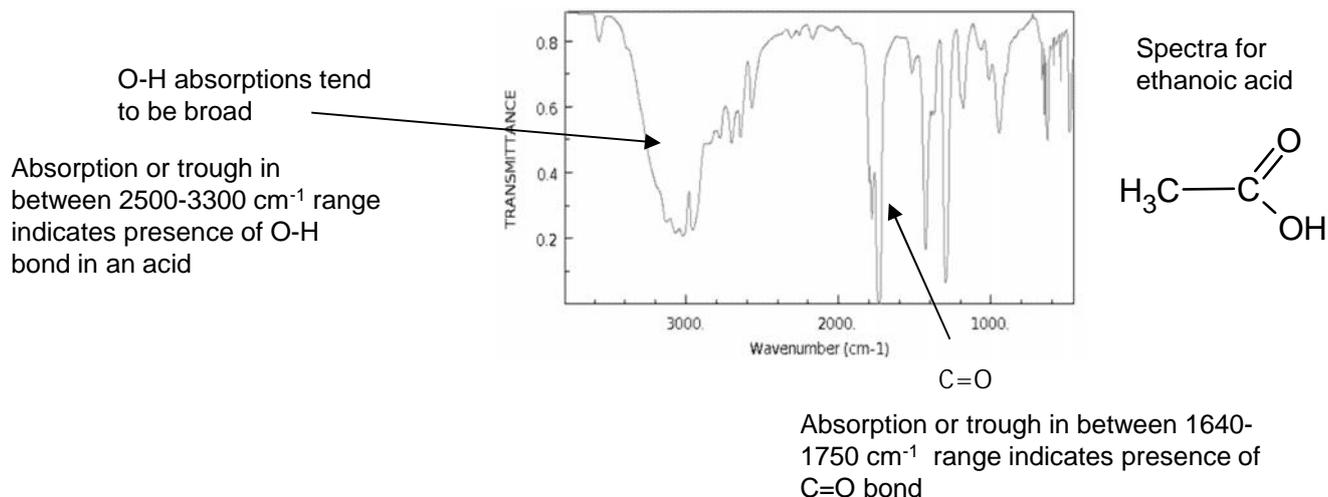
Molecules which change their polarity as they vibrate can absorb infrared radiation. E.g. C-H, C=O, O-H

Molecules such as H_2, O_2 and N_2 cannot change their polarity as they vibrate so can absorb infrared radiation and don't register on an infra red spectrum

The absorption of infra-red radiation by bonds in this type of spectroscopy is the same absorption that bonds in CO_2, methane and water vapour in the atmosphere do that cause them to be greenhouse gases.

H_2O, CO_2, CH_4 and NO molecules absorb IR radiation and are greenhouse gases, whilst O_2 and N_2 are not.