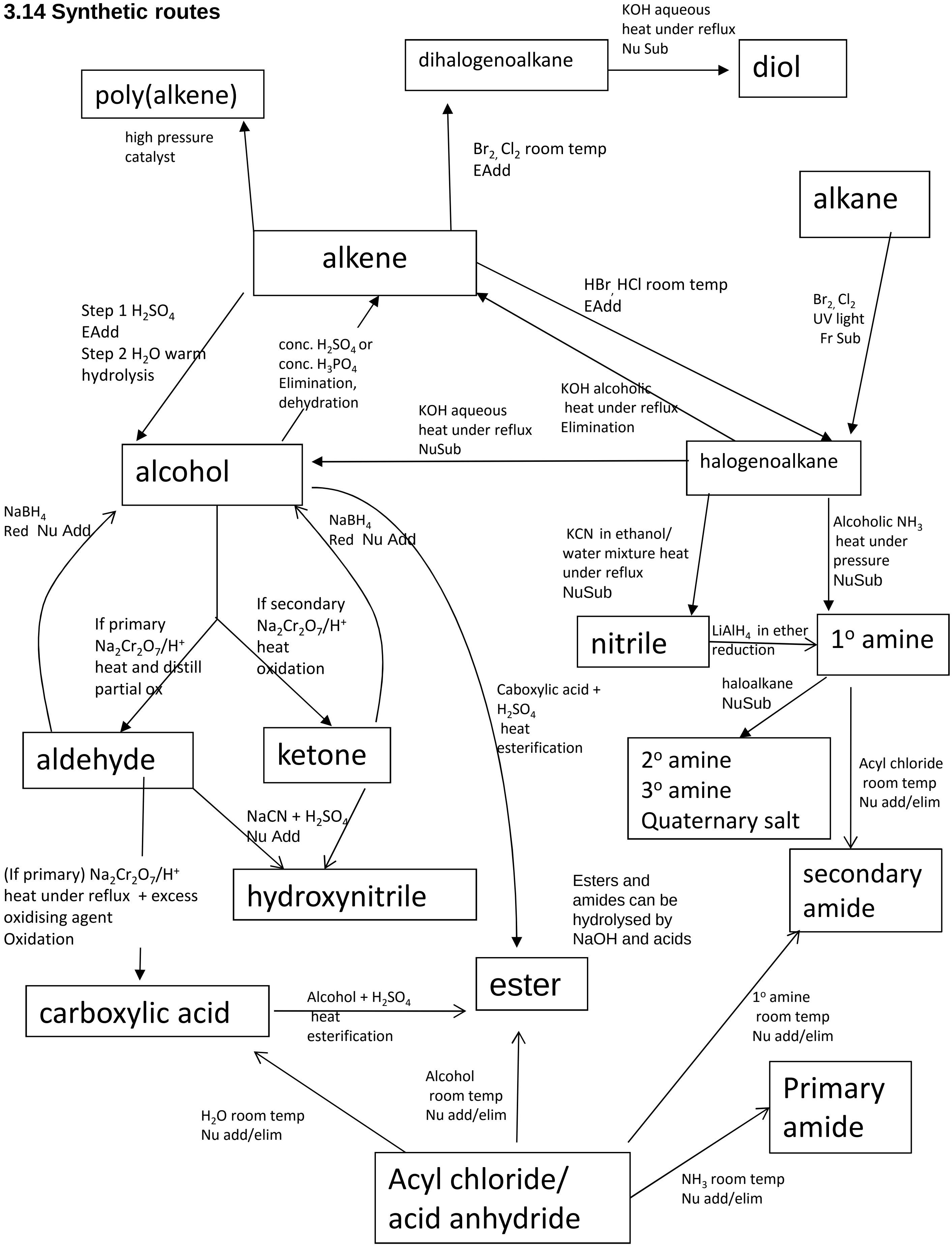
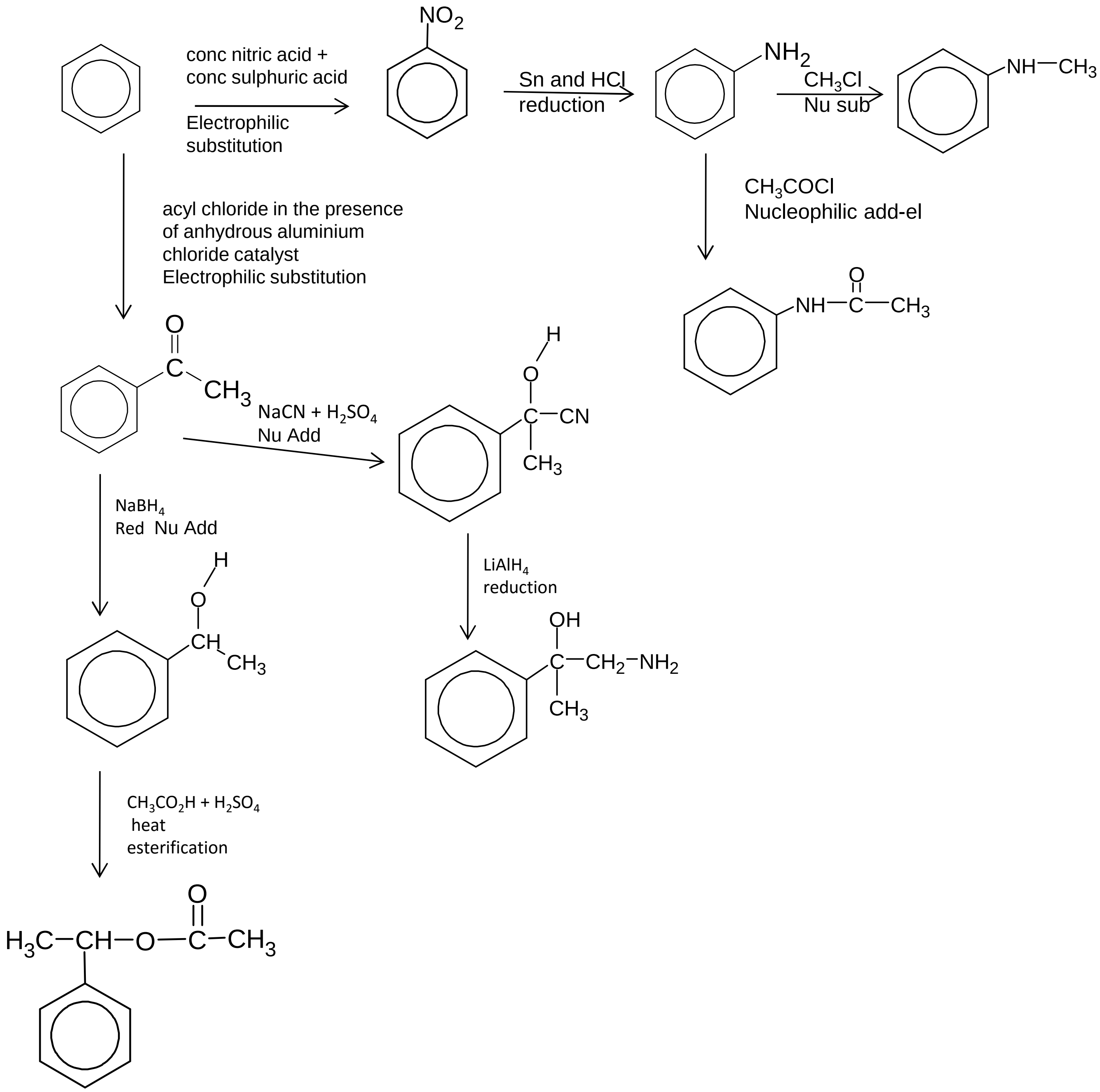
3.14 Synthetic routes



Aromatic synthetic routes

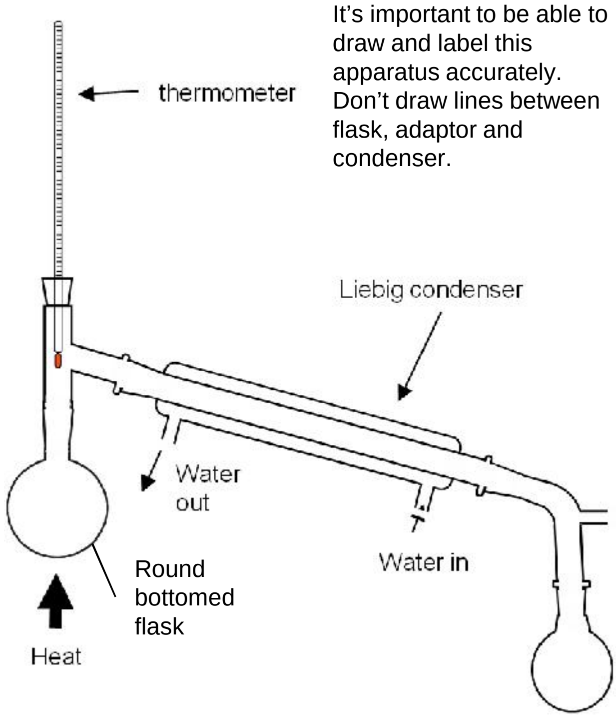


Organic techniques

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.

Classic AS reaction using distillation
Reaction: primary alcohol → aldehyde
Reagent: potassium dichromate (VI) solution and dilute sulphuric 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



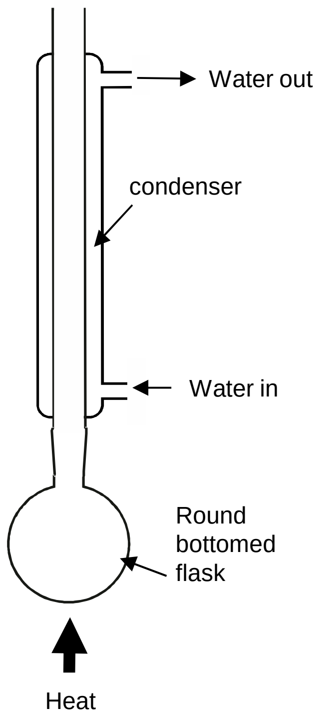
It's important to be able to draw and label this apparatus accurately. Don't draw lines between flask, adaptor and condenser.

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.

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 AS reaction using reflux
Reaction: primary alcohol → carboxylic acid
Reagent: potassium dichromate(VI) solution and dilute sulphuric acid
Conditions: use an excess of dichromate, and **heat under reflux**: (distill 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



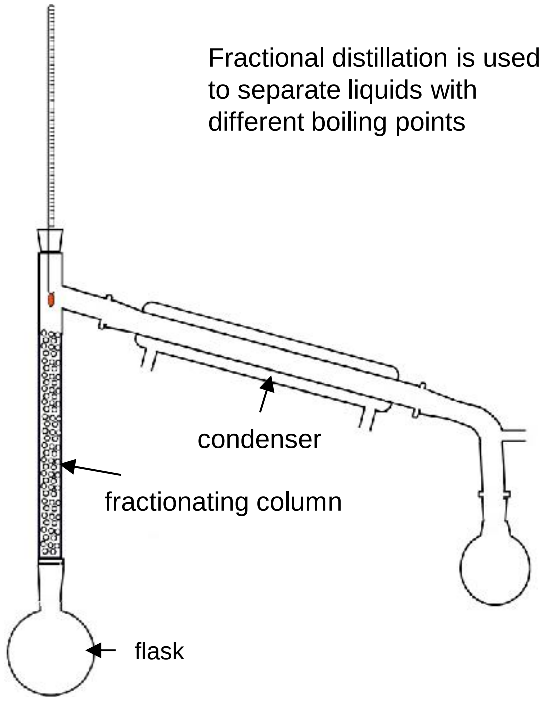
Anti-bumping granules are added to the flask in both distillation and reflux to prevent vigorous, uneven boiling by **making small bubbles** form instead of large bubbles

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

Fractional Distillation: In the laboratory

- Heat the flask, with a Bunsen burner or electric mantle
- This causes vapours of all the components in the mixture to be produced.
- Vapours pass up the fractionating column.
- The vapour of the substance with the lower boiling point reaches the top of the fractionating column first.
- The thermometer should be at or below the boiling point of the most volatile substance.
- The vapours with higher boiling points condense back into the flask.
- Only the most volatile vapour passes into the condenser.
- The condenser cools the vapours and condenses to a liquid and is collected.

Fractional distillation is used to separate liquids with different boiling points



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.

Purifying an organic liquid

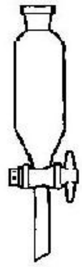
- Put the distillate of impure product into a separating funnel
- wash product by adding either
  - sodium hydrogencarbonate solution , shaking and releasing the pressure from CO_2 produced.
  - Saturated sodium chloride solution
- Allow the layers to separate in the funnel, and then run and discard the aqueous layer.
- Run the organic layer into a clean, dry conical flask and add three spatula loads of drying agent (anhydrous sodium sulphate) to dry the organic liquid.
- Carefully decant the liquid into the distillation flask
- Distill 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



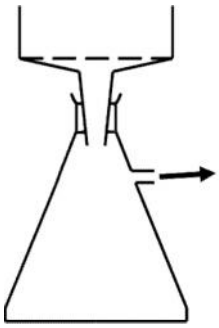
Purifying an organic solid: Recrystallisation

Used for purifying aspirin

Step	Reason
1. Dissolve the impure compound in a **minimum volume** of **hot** (near boiling) **solvent**.	An appropriate solvent is one which will dissolve both compound and impurities when hot **and** one in which the compound itself does not dissolve well when cold. The minimum volume is used to obtain saturated solution and to enable crystallisation on cooling
2. **Hot filter** solution through (fluted) filter paper quickly.	This step will remove any insoluble impurities and heat will prevent crystals reforming during filtration
3. **Cool** the filtered solution by inserting beaker **in ice**	Crystals will reform but soluble impurities will remain in solution form because they are present in small quantities so solution is not saturated. Ice will increase the yield of crystals
4**. Suction filtrate** with a Buchner flask to separate out crystals	The water pump connected to the Buchner flask reduces the pressure and speeds up the filtration.
5 Wash the crystals with distilled water	To remove soluble impurities
6. Dry the crystals between absorbent paper	

Loss of yield in this process
- Crystals lost when filtering or washing
- Some product stays in solution after recrystallisation
- other side reactions occurring

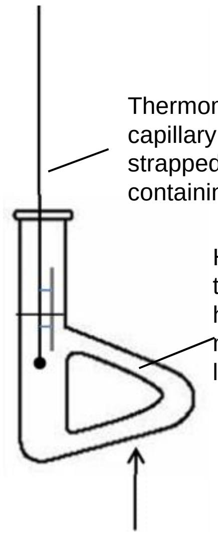
buchner flask



Measuring melting point

One way of testing for the degree of purity is to determine the melting "point", or melting range, of the sample.

If the sample is very pure then the melting point will be a sharp one, at the same value as quoted in data books.



If **impurities** are present (and this can include solvent from the recrystallisation process) the **melting point will be lowered** and the sample will **melt over a range** of several degrees Celsius

Melting point can be measured in an electronic melting point machine or by using a practical set up where the capillary tube is strapped to a thermometer immersed in some heating oil.

In both cases a small amount of the salt is put into a capillary tube. The tube is heated up and is **heated slowly near the melting point**

Comparing an experimentally determined melting point value with one quoted in a data source will verify the degree of purity.

Sometimes an error may occur if the temperature on the thermometer is not the same as the temperature in the actual sample tube.

Testing for Organic Functional Groups

Functional group	Reagent	Result
Alkene	Bromine water	Orange colour decolourises
Aldehyde	Fehlings solution	Blue solution to red precipitate
Aldehyde	Tollens Reagent	Silver mirror formed
Carboxylic acid	Sodium carbonate	Effervescence of CO_2 evolved
1° 2° alcohol and aldehyde	Sodium dichromate and sulphuric acid	Orange to green colour change
chloroalkane	Warm with silver nitrate	Slow formation of white precipitate of AgCl
Acyl chloride	Silver nitrate	Vigorous reaction- steamy fumes of HCl- rapid white precipitate of AgCl

Tollen's Reagent

Reagent: Tollen's Reagent formed by mixing aqueous ammonia and silver nitrate. The active substance is the complex ion of $[Ag(NH_3)_2]^+$.

Conditions: heat gently

Reaction: aldehydes only are oxidised by Tollen's reagent into a carboxylic acid and the silver(I) ions are reduced to silver atoms

Observation: with aldehydes, a silver mirror forms coating the inside of the test tube. Ketones result in no change.

$$CH_3CHO + 2Ag^+ + H_2O \rightarrow CH_3COOH + 2Ag + 2H^+$$

Fehling'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 and the copper 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

$$2CH_3CO_2H + Na_2CO_3 \rightarrow 2CH_3CO_2^-Na^+ + H_2O + CO_2$$