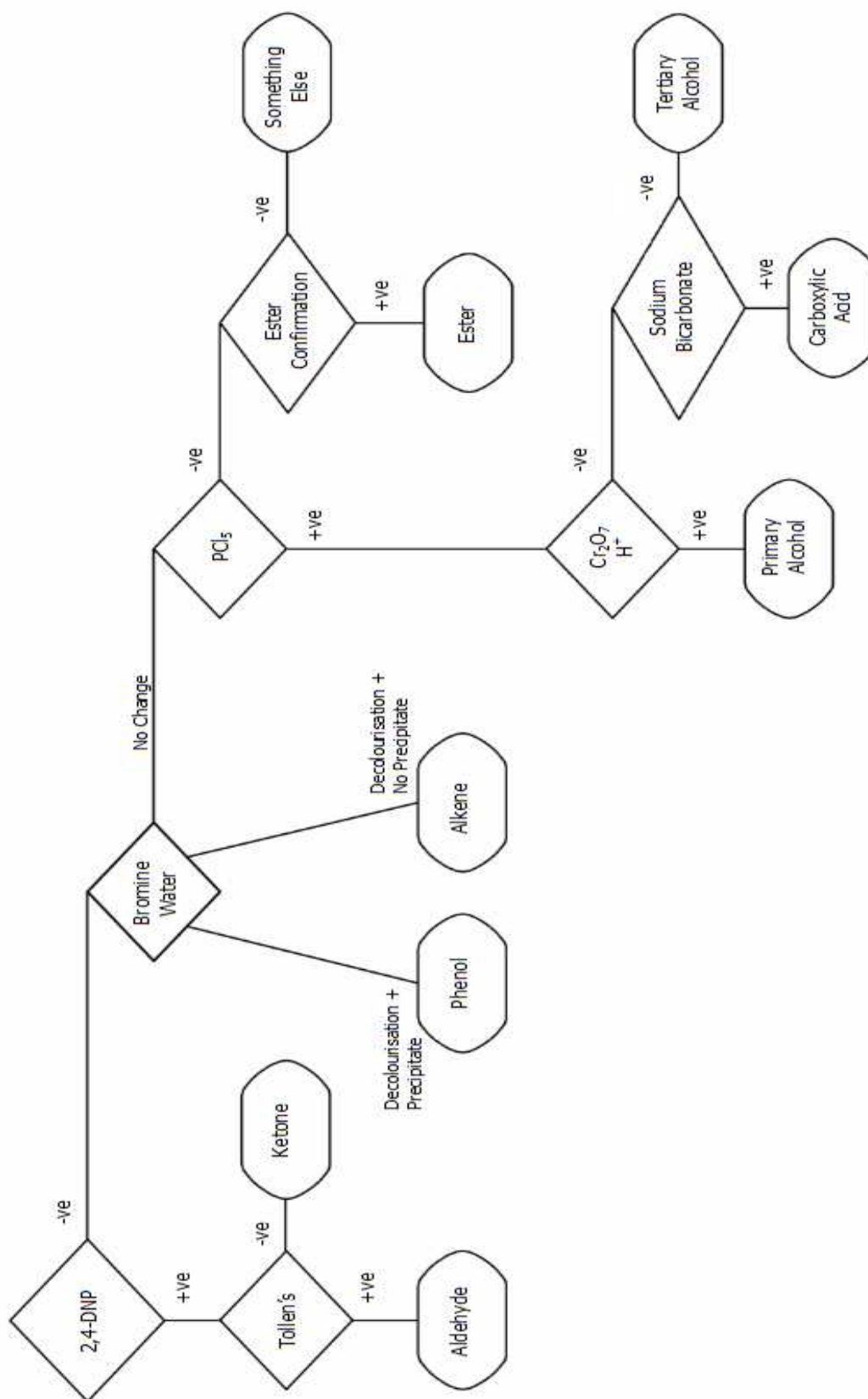


## Identification of an organic unknown

Here is the flow chart to determine the unknown organic. Start with the 2,4-DNP test and then follow the chart.



## DNP - 2,4-dinitrophenylhydrazine test

The Safety:

- DNP is harmful – avoid contact with skin, eyes etc. Wear safety glasses.
- At this stage we have no idea what the organic chemical to be tested is, so wear gloves.

The Instructions:

To 1cm<sup>3</sup> of 2,4-dinitrophenylhydrazine (DNP) solution, add a few drops of the unknown organic substance.

If a yellow/orange precipitate is formed, it indicates the presence of a carbonyl group (aldehyde or ketone) (**positive** result). Move on to the **Tollen's reagent test**.

If no precipitate is formed (**negative** result), move on to the **Bromine water test**.

The Chemistry:

2,4-dinitrophenylhydrazine bonds to carbonyl compounds and makes an orange precipitate. The reaction also releases water.

## Tollen's reagent test

The Safety:

- Silver nitrate is poisonous and harmful, particularly to the eyes and nose. It will stain skin.
- Sodium hydroxide is an irritant when dilute.
- Aldehydes and ketones may be toxic.
- Silver metal poses little threat.
- Ammonia in solution is particularly damaging to the eyes, besides being toxic if swallowed and harmful to the skin.
- Wear goggles and gloves, avoid contact with chemicals.

The Instructions:

Tollen's reagent must be prepared within a couple of hours of use. Preparation instructions for testing one chemical:

- Add a drop of dilute NaOH to 1cm<sup>3</sup> of AgNO<sub>3</sub>. A brown precipitate (silver oxide) will form.
- Add concentrated NH<sub>3</sub> until the precipitate just dissolves.

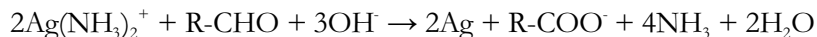
Add a few drops of the carbonyl compound to the prepared Tollen's reagent in a test tube. Leave it in a hot water bath for a few minutes.

If a "silver mirror" (or merely a silver precipitate) forms on the test tube, it is an indication that an **aldehyde** is present (**positive**).

Otherwise (**negative**), the unknown chemical is a **ketone**.

The Chemistry:

Tollen's reagent is an oxidising agent, and will oxidise an aldehyde to a carboxylic acid. Ketones won't be oxidised.



The silver ions are reduced to silver metal.

## Bromine water test

The Safety:

- Bromine water is corrosive and harmful.
- Phenol is toxic and corrosive.
- Alkenes are likely to be highly flammable, and may be harmful.
- 2,4,6-tribromophenol is an irritant.
- Halogenoalkanes may be toxic and harmful.
- Wear safety glasses and gloves, avoid contact with chemicals. Work in a well-ventilated area away from any open flames.

The Instructions:

Add excess bromine water to 1cm<sup>3</sup> of the unknown chemical in a test tube, and shake.

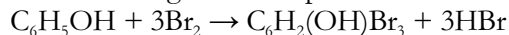
If the bromine water is decolourised from orange/brown to colourless with a white precipitate produced, **phenol** is present.

If the bromine water is decolourised but no white precipitate is present, the unknown is an **alkene**.

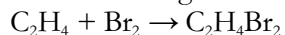
If there is **no change**, neither phenol nor an alkene is present, so move on to the **PCl<sub>5</sub> test**.

The Chemistry:

Phenol undergoes electrophilic substitution with the bromine:



Alkenes undergo electrophilic addition with the bromine:



### **PCl<sub>5</sub> test**

The Safety:

- PCl<sub>5</sub> reacts violently with water – keep away from any moisture. Harmful, corrosive.
- HCl fumes are toxic and corrosive.
- Alcohols can be harmful and are probably flammable.
- Esters may be harmful.
- Carboxylic acids can be corrosive and harmful.
- Wear gloves and goggles. Work in a fume cupboard. Keep away from water and fire.

The Instructions:

Place 0.5cm<sup>3</sup> of the unknown into a dry test tube, and add 0.1g of phosphorus pentachloride. Blow gently across the top of the test tube to see whether a gas has been produced.

If white fumes (HCl) are evolved, the organic compound contains an OH group (**positive** result). Move on to the **acidified dichromate test**.

If no fumes are released (**negative** result), proceed to the **phenolphthalein ester confirmation test**.

The Chemistry:

PCl<sub>5</sub> reacts readily with any OH group, producing HCl and replacing the OH group with a Cl.

### **Phenolphthalein ester test**

The Safety:

- Phenolphthalein is a slight irritant and possible carcinogen.
- Dilute sodium hydroxide is an irritant
- Ethanol is harmful and highly flammable. Resist temptation to drink.
- Esters may be harmful.
- Wear safety glasses. Keep ethanol well away from any flames.

The Instructions:

Mix approximately 1cm<sup>3</sup> of the unknown chemical in a test tube with a squirt of ethanol or water and a couple of drops of phenolphthalein. Add a few drops of dilute NaOH until the indicator turns pink.

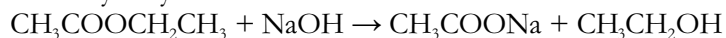
Gently heat the test tube. If the indicator changes back to being colourless, the test is **positive** for an **ester**.

Otherwise, the unknown chemical remains **unknown** and further testing is required.

The Chemistry:

Phenolphthalein is an indicator for alkalis. The NaOH turns the phenolphthalein pink. When the ester is heated, it hydrolyses into an acid and an alcohol. This acid reacts with the NaOH, returning the solution to neutral or acidic, and the indicator changes back to colourless.

Alkali hydrolysis of esters:



## Acidified dichromate test

The Safety:

- Potassium dichromate is nasty. Don't get it in your eyes! Corrosive, causes burns, known carcinogen.
- Sulphuric acid is corrosive and toxic.
- Alcohols can be harmful and are probably flammable.
- Carboxylic acids can be corrosive and harmful.
- Wear goggles and gloves.

The Instructions:

Mix equal quantities of roughly 0.1M potassium dichromate solution and 1M sulphuric acid. This should be an orange colour.

Take about 1cm<sup>3</sup> of the organic unknown in a test tube and add a few drops (0.1cm<sup>3</sup>) of the above mixture. Warm gently.

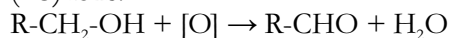
A **positive** result is indicated by a change in colour from orange to green. If this is the case, the unknown chemical is a **primary alcohol**.

If the mixture doesn't change colour, the test is **negative**. Proceed to the **sodium bicarbonate test**.

The Chemistry:

Acidified potassium dichromate is an oxidising agent, and will oxidise a primary alcohol to an aldehyde or carboxylic acid. Tertiary alcohols and carboxylic acids won't be oxidised.

In oxidising the alcohol, the orange-coloured chromium (+6) ions will be reduced to green chromium (+3) ions.



## Sodium bicarbonate test

The Safety:

- Sodium bicarbonate is a mild irritant to the eyes.
- Lime water (Calcium Hydroxide solution) is corrosive and an irritant.
- CO<sub>2</sub> poses no risk.
- Alcohols can be harmful and are probably flammable.
- Carboxylic acids can be corrosive and harmful.
- Wear safety glasses.

The Instructions:

Take roughly 1cm<sup>3</sup> of the unknown in a test tube and add about one spatula of sodium bicarbonate powder, a little at a time.

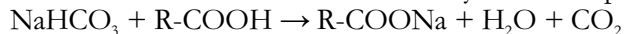
Effervescence (CO<sub>2</sub> gas evolved) indicates a **positive** result - the unknown is a **carboxylic acid**.

If no gas is produced (**negative** result), the unknown is a **tertiary alcohol**.

If necessary, the gas can be bubbled through lime water to confirm that it is actually CO<sub>2</sub>, which will turn the lime water cloudy.

The Chemistry:

Sodium bicarbonate reacts with carboxylic acids to produce a salt, water, and carbon dioxide.



## References

OCR Chemistry 2/ISBN 0-521-79882-5/ Pages 7, 16, 21-31 and 50

<http://www.jtbaker.com/msds/englisbhtml/d746a.htm> etc.

<http://msds.chem.ox.ac.uk/PH/phenol.html> etc.

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