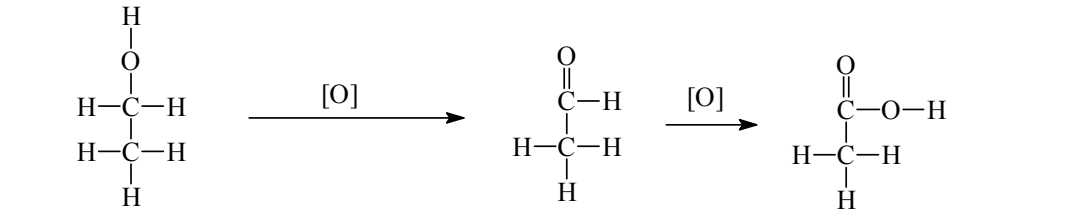
The oxidation-reduction reactions of carbonyl compounds

Oxidation

Aldehydes can be easily oxidised to carboxylic acids.

This oxidation from primary alcohols is a two stage process.



ethanol (primary alcohol)

ethanal (aldehyde)
This needs to be distilled off before further oxidation

ethanoic acid (carboxylic acid)

This is more simply represented as:

$$\underset{\text{Aldehyde}}{RCHO} + [O] \xrightarrow[\text{reflux}]{K_2Cr_2O_7(aq)/H^+(aq)} \underset{\text{Carboxylic Acid}}{RCOOH}$$

Ketones cannot be oxidised without the molecule being broken up.

Aldehydes are powerful reducing agents possible to:

- Reduce copper 2+ to copper (I)
- Silver (I) to metallic silver

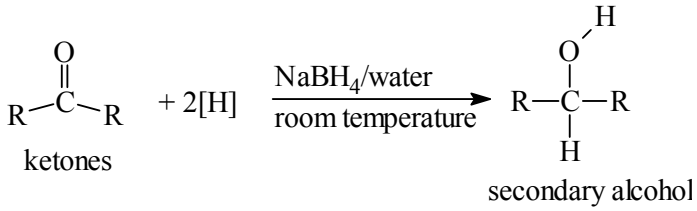
There are used as a basis to distinguish aldehydes from ketones.

Reduction

It is possible to make primary and secondary alcohols by reduction of aldehydes and ketones.

Aldehydes give 1° alcohols and ketones 2° alcohols.

$$\underset{\text{Aldehyde}}{RCHO} + 2[H] \xrightarrow[\text{room temperature}]{NaBH_4/\text{water}} \underset{\text{Primary alcohol}}{RCH_2OH}$$



ketones

secondary alcohol

Other reducing agents include:

- Lithium tetrahydridoaluminate (III) $LiAlH_4$ needs to be in ethoxyethane – water eliminated.
- Sodium in ethanol
- Hydrogen gas under pressure with platinum catalyst

Remember: Oxidising agents maybe written as [O] and reducing agents [H]. Remember to balance these equations even when using these symbols

Questions

1. Write balanced equations (using [H]) for the reaction of sodium tetrahydridoaluminate (III) in water with
   a) CH_3CHO
   b) $CH_3CH_2COCH_3$
   c) CH_3COCH_2CHO

2. How would you expect each of the following compounds A, B and C, to react:
   a) when refluxed with acidified potassium dichromate (VI) solution
   b) with sodium tetrahydridoaluminate (III) in water

   A – CH_3CH_2CHO
   B – $(CH_3)_2CHOH$
   C – CH_3COCH_3

3 2-Oxopropanal, CH_3COCHO, is thought to be one of the chemicals responsible for the smell in burnt sugar
   a) This compound contains two carbonyl groups. Explain the difference between the two groups.
   b) What reagent(s) would you use to reduce this compound?
   c) Draw the full displayed formula of the compound formed in the reduction reaction.
   d) If the oxopropanal is reluxed with potassium dichromate (VI) solution, a new compound is formed. Write an equation, using [O] where appropriate.

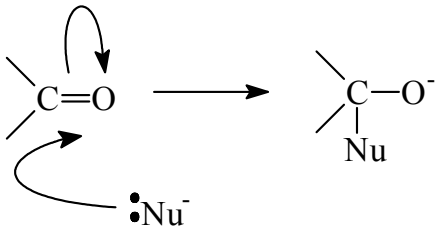
Nucleophilic addition to the carbonyl bond

Alkenes undergo electrophilic addition, and due to the high electron density round the carbonyl bond they could be expected to undergo the same. The situation is however very different.

- Oxygen is electronegative (more so than carbon)
- Pulls electron density away from the carbon so that the bond is polar.

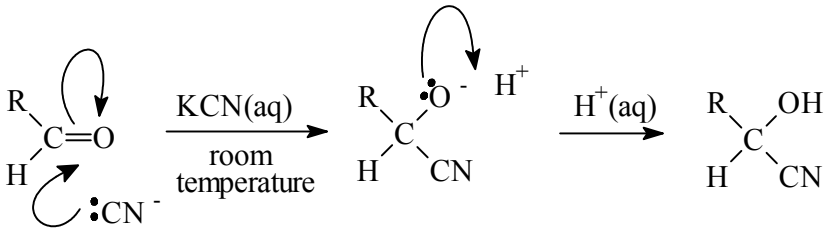
This partial withdrawal of electron density from the carbon exposes it to attack by negatively charged nucleophiles.

Nucleophiles are often negatively charged (CN^-), but sometimes are neutral molecules with a lone pair of electrons e.g. $:NH_3$.



The board specifies that you know the Nucleophilic reaction of hydrogen cyanide with ketones an aldehydes.

- Hydrogen cyanide (HCN) is too toxic to use, so potassium or sodium cyanide is used with a mixture of sulphuric or hydrochloric acid.



a 2-hydroxynitrile

This mechanism needs to be committed to memory – yes learnt like a parrot!
Quote from board, *'Candidates should show 'curly arrows' relevant lone pairs and dipoles in this mechanism'.*

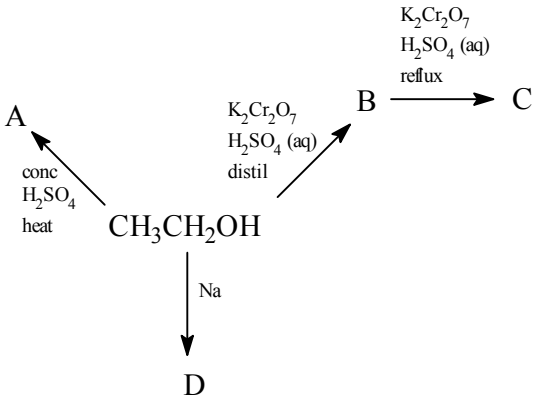
So insert those dipoles now!!!

Nitriles can be hydrolysed to carboxylic acids by refluxing with dilute hydrochloric acid. This gives a way of synthesising 2-hydroxycarboxylic acids.

Perhaps the most important is 2-hydroxypropanoic acid – lactic acid. A product of anaerobic respiration. Important as an introduction to optically active compounds – chirality.

Questions

1 Complete the following reaction sequence by identifying compounds A, B, C and D.



2 Consider the following series of compounds

A $CH_3CH_2CH_2COCH_3$
B $CH_3CH(OH)CH_2COCH_3$
C CH_3CH_2CHO
D $CH_3COCH_2COCH_3$

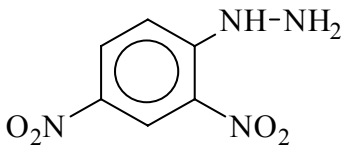
a) Write the systematic name for each of these compounds.
b) Which of these compounds are alcohols?
c) Which of these compounds are aldehydes?
d) Which of these compounds are ketones?
e) Which could be formed by the oxidation of a primary alcohol?
f) Which can be reduced to a secondary alcohol?

3 Write a mechanism to show how HCN undergoes nucleophilic addition to $CH_3CH_2COCH_2CH_3$.

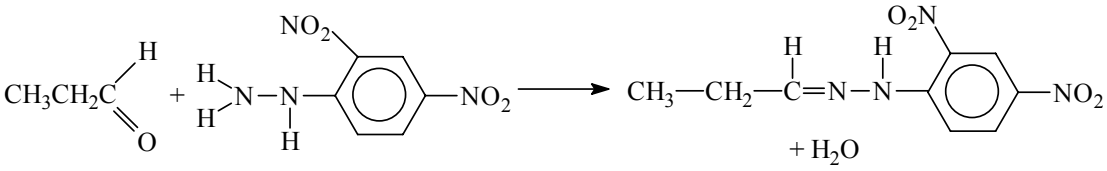
Condensation reactions of the carbonyl bonds

Based on ammonia or more specifically hydrazine $H_2N\text{-}NH_2$ adds across the carbonyl bond. The addition is immediately followed by loss of water. This addition-elimination is called a condensation reaction

The most important of these is the reaction of carbonyls with 2,4-dinitrophenylhydrazine (2,4-DNPH).



This reaction occurs as follows:



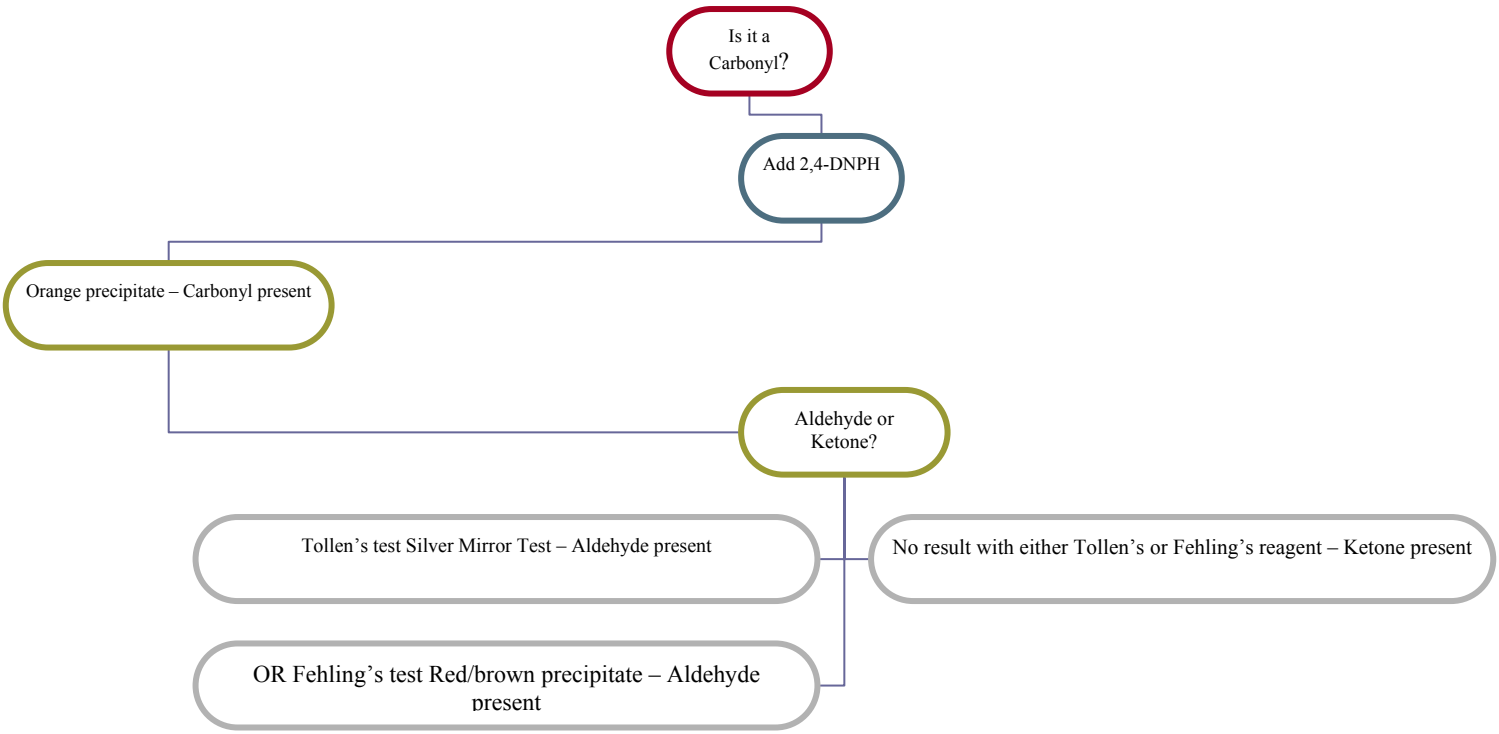
This substituted 2,4-dinitrophenylhydrazone produces a precipitate of orange crystals. These are essential in identifying unknown carbonyl.

- React unknown with 2,4-DNPH, orange ppte formed
- Filter and recrystalise the orange crystals, dry thoroughly.
- Find melting point of crystals, this will be sharp is crystals are pure
- Look up in melting point tables to identify the unknown carbonyl.

This is important – the exam board expect you to be able to reproduce this. You do not have to learn the equation of this reaction – shame as it is not hard!

Testing for aldehydes and ketones

Distinguishing between carbonyls and other organic compounds is quite easy, simply add 2,4-DNPH as above. The trick is to distinguish between aldehydes and ketones themselves.



Tollens' Test

Simply put, this uses the reducing power of aldehydes to reduce silver (I) to metallic silver. This is seen as a silver mirror on the inside of the test tube. Hence the test is often known as the silver mirror test.

The creation of the reagent in this case is quite complex:

- Ag^+ has to be in alkaline solution for this reaction to occur
- Addition of hydroxide ions (OH^-) precipitates silver oxide (Ag_2O)
- Ammonia is the complexing agent

1. Add ammonia carefully to about $3cm^3$ of silver nitrate in a clean test tube
2. Stop adding drops when the precipitate is just redissolved
3. Careful when adding ammonia – XS is not good!

This clear solution now contains the complex ion $[Ag(NH_3)_2]^+$.

- A couple of drops of the aldehyde are added to the clear solution
- The solution is warmed gently in warm water

A positive result = silver mirror. A dirty test tube will give a black or grey ppte.

$$CH_3CH_2CHO + [O] \rightarrow CH_3CH_2COOH$$

$$2[Ag(NH_3)_2]^+(aq) + H_2O(l) \rightarrow 2Ag(s) + [O] + 2NH_4^+(aq) + 2NH_3(aq)$$