WJEC Chemistry A-Level

OA2.2: Aldehydes and Ketones

Detailed Notes

English Specification

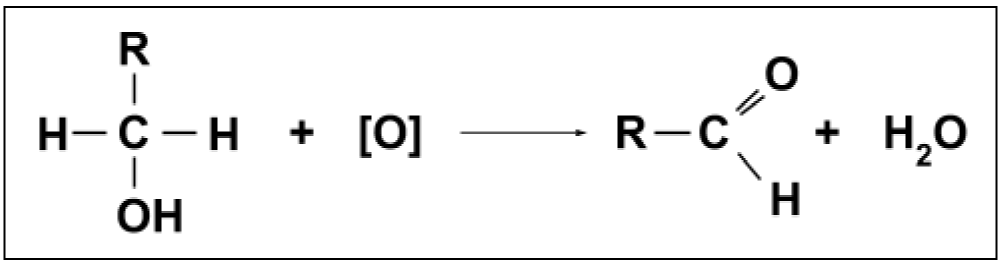
Aldehydes

Aldehydes are organic compounds, recognised by the functional group **-CHO.** They contain a **carbonyl group (C=O)** where the carbon atom in the carbonyl group is bonded to, at most, one other carbon atom.

Aldehydes can be produced from the initial **oxidation and distillation of primary alcohols**.

To oxidise a primary alcohol to an aldehyde, **acidified potassium dichromate(VI)** or **acidified potassium manganate(VII)** is used as an **oxidising agent**.

Example:



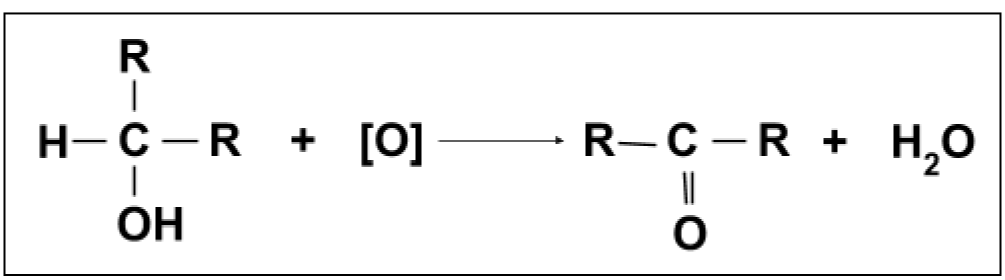
The product must be **distilled** immediately to obtain the aldehyde, otherwise further oxidation of the aldehyde will produce a **carboxylic acid**.

Ketones

Ketones are also recognised by the **carbonyl group** -C=O. They **differ from aldehydes** as the carbon atom in the carbonyl group is bonded to **two other carbon atoms**.

Ketones are produced from the **oxidation of secondary alcohols.** As with aldehydes, **acidified potassium dichromate(VI)** or **acidified potassium manganate(VII)** is used as an **oxidising agent**.

Example:



Unlike with aldehydes, **no further oxidation** of the ketone occurs.

Testing for aldehydes and ketones

Oxidation colour change

When primary alcohols and secondary alcohols are oxidised to aldehydes and ketones using acidified **potassium dichromate(VI)**, the solution will **change colour** from **orange** to **green**. This is because the orange **dichromate(VI)** ion is reduced to a green **chromium(III)** ion.

If acidified **potassium manganate(VII)** is used as the oxidising agent, the purple solution will decolourise as the manganate(VII) ion is reduced.

Tollen's Reagent

Tollen's reagent can be used to **distinguish** between an **aldehyde or ketone**.
When Tollen's reagent is added to an **aldehyde**, a **silver mirror** forms on the inside of the test tube. When Tollen's reagent is added to a **ketone**, **no reaction** takes place.

Fehling's Reagent

Fehling's reagent can also be used to **distinguish** between an **aldehyde or ketone**. Fehling's reagent is a **blue solution**.
When Fehling's reagent is added to an **aldehyde**, the blue solution gives a brick red precipitate. When Fehling's reagent is added to a **ketone**, **no reaction** takes place and the solution **remains blue**.

Iodoform Test

Iodine and **sodium hydroxide** solution can be combined as the reagents for this chemical test. It allows the presence of a **CH_3CO group** to be identified.

In the test, a small amount of iodine solution is added followed by just enough sodium hydroxide to **remove the colour of the iodine**. If this CH_3CO group is present, a **pale yellow precipitate** of triiodomethane (iodoform) is produced.

Reduction Reactions

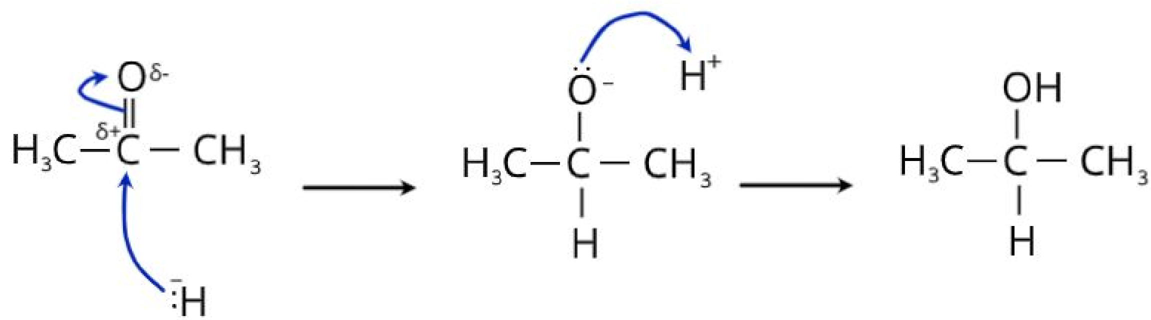
All of the oxidation reactions involved in the production of aldehydes and ketones can be reversed to reproduce the alcohols. These reactions are called **reduction reactions**. For this, a reducing agent of **$NaBH_4$** (dissolved in water with methanol) is used and the mechanism is an example of **nucleophilic addition**.

$$CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$$

The reducing agent $NaBH_4$ provides the **H:⁻ nucleophile**. However, a H^+ ion is also required so the reaction takes place under **aqueous conditions** so that the water molecules can provide this ion.

The mechanism is the same for the reduction of **aldehydes** to **primary alcohols**.

Mechanism

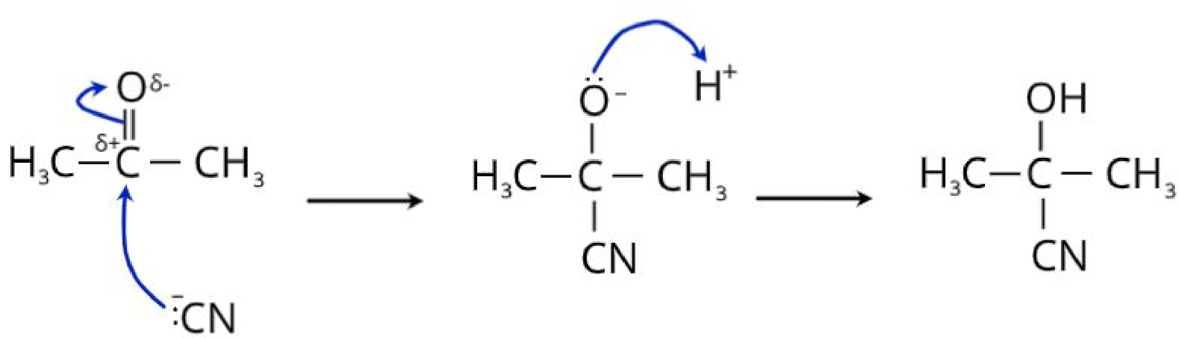


Hydroxynitriles

Nucleophilic addition reactions are characteristic of aldehydes and ketones, especially those with the :CN⁻ nucleophile. Reaction with a cyanide ion is a form of **organic synthesis** as it causes an **extension of the carbon chain** by one carbon atom. The product of the reaction is a **hydroxynitrile**.

KCN (potassium cyanide) is often used as the reagent to provide the nucleophile instead of HCN (hydrogen cyanide). This is because **HCN** is a highly **toxic gas** and is **difficult to store**.

Mechanism - nucleophilic addition of propanone with hydrogen cyanide to produce 2-hydroxypropanenitrile



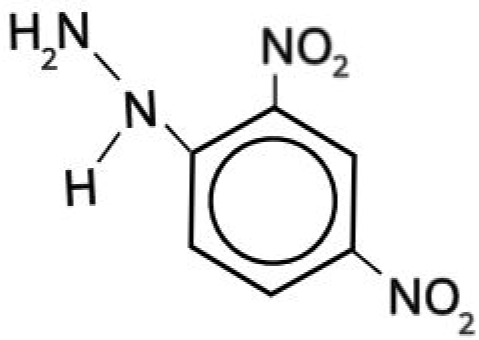
Hydroxynitriles commonly contain a **chiral carbon centre** meaning optical isomers of the product exist. In the above mechanism, the :CN- nucleophile can attack from either above or below the **planar double bond**, producing the two different **enantiomers**.

Hydroxynitriles can undergo **hydrolysis** to form important **hydroxyacids** which are commonly used in **skincare products** and the **cosmetics industry**.

Tests for Aldehydes and Ketones

2-4-DNP

This molecule consists of nitrogen, hydrogen and a benzene ring with **substituted nitro groups**. It is often abbreviated to 2-4-DNP.



As a molecule, it can react with aldehydes and ketones via an **addition-elimination** reaction to produce **2-4-dinitrophenylhydrazone compounds**. This can also be considered as a condensation reaction as the two molecules involved combine and expel water as a byproduct.

Therefore, 2-4-DNP can be used as a **test for aldehydes and ketones**. If a carbonyl **-C=O** group is present, an **orange-yellow precipitate** will form.

2,4-DNP can also be used to **identify specific aldehydes and ketones**:

1. First add 2,4-DNP so that a precipitate forms.
2. Purify the solid by method of **recrystallisation**.
3. **Compare** the **melting point** of the pure crystals formed with the melting points of **2,4-dinitrophenylhydrazones** of all the common aldehydes and ketones.