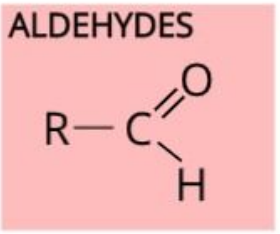
CIE Chemistry A Level

18 : Carbonyl Compounds

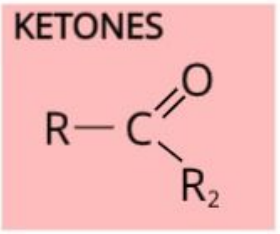
Notes

Aldehydes and Ketones

Aldehydes and **ketones** both contain the carbonyl group, C=O.
The **position** of the **carbonyl** group in the carbon chain is **different** in aldehydes and ketones.



The carbonyl group is at the end of the carbon chain in aldehydes and in the middle in ketones. The suffix for aldehydes is **-al** and the suffix for ketones is **-one**.



Formation of aldehydes and ketones

Aldehydes and ketones are formed when alcohols are **oxidised** using **acidified potassium dichromate(VI)** ($Cr_2O_7^{2-}/H^+$).

Aldehydes are formed from **primary** alcohols, whereas ketones are formed from **secondary** alcohols.

Primary alcohols

Primary alcohols can be **partially oxidised** to **aldehydes**.

$$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$$

If the aldehyde undergoes **further oxidation**, **carboxylic acids** are produced.

$$CH_3CHO + [O] \rightarrow CH_3COOH + H_2O$$

The full oxidation reaction can be written as:

$$CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + 2H_2O$$

If you are only collecting the aldehyde, carry out the reaction with excess alcohol and distill off the aldehyde as soon as it forms to prevent further oxidation.

Secondary alcohols

Secondary alcohols are oxidised to **ketones**. No further oxidation can take place.

$$CH_3C(OH)HCH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$$

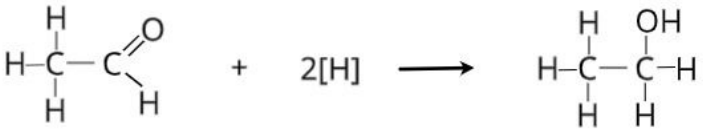
Reduction of aldehydes and ketones

A **reducing agent** can be used to reverse the reactions above and convert aldehydes and ketones back to primary and secondary alcohols.
Typically $LiAlH_4$ or $NaBH_4$ (dissolved in water with methanol) are used as reducing agents for this reaction.

Reduction of aldehydes

$$RCHO + 2[H] \rightarrow RCH_2OH$$

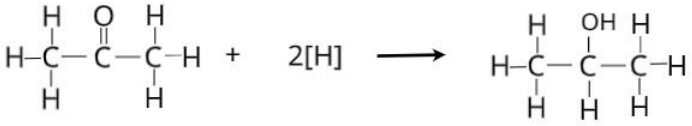
For example, the reduction of **ethanal to ethanol**:



Reduction of ketones

$$R_1COR_2 + 2[H] \rightarrow RC(OH)HR_2$$

For example, the reduction of **propanone to propanal**:

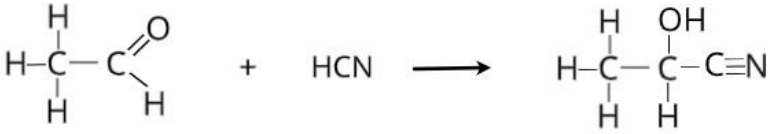


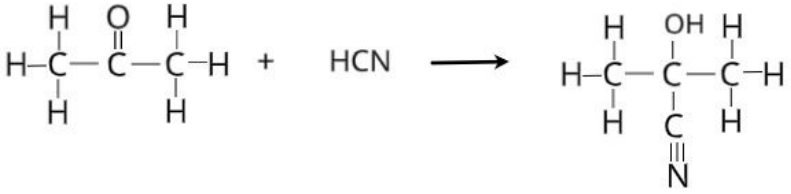
Reaction with HCN and KCN or NaCN

Hydrogen cyanide reacts with aldehydes and ketones to produce **hydroxynitrile compounds** by removing the C=O double bond. The reaction is called **nucleophilic addition** (see the mechanism on the following page).

Naming:

When naming a hydroxynitrile, the **carbon in the nitrile group (C≡N)** is referred to as the **first carbon** so the position of groups (including the alcohol group) is counted from there. In the equations below, the product of the first reaction is **2-hydroxypropanenitrile** and the product of the second reaction is **2-hydroxy-2-methylpropanenitrile**.





HCN is a very **poisonous gas.** Often **KCN** or **NaCN** are used with acid instead to form HCN in situ.

Nucleophilic addition reactions

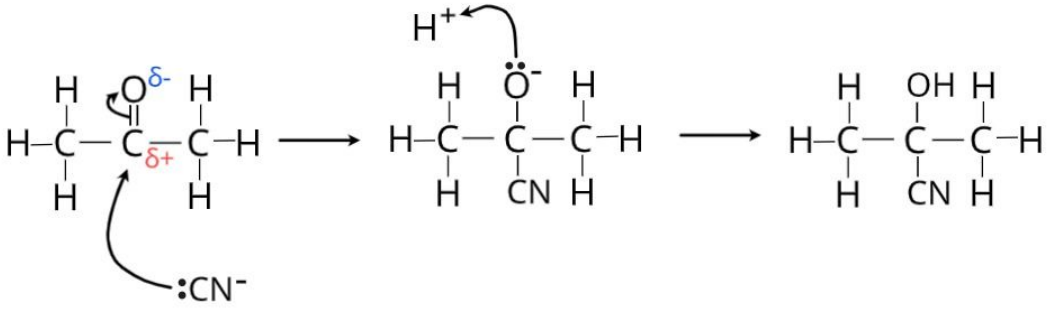
When aldehydes and ketones react with HCN to form **hydroxynitriles**, a **nucleophilic addition** reaction occurs.

A nucleophile is an **electron pair donor**.

The mechanism:

The **carbonyl bond** (C=O) is **highly polar**. The negative **cyanide ion** acts as a **nucleophile** and attacks the slightly positive carbon atom. The C=O bond breaks, leaving only a **single bond** between the **carbon and oxygen** atoms.

The negatively charged oxygen then bonds to a **hydrogen ion** (from HCN or any added acid).



Detecting carbonyl compound

The carbonyl group can be detected using 2,4-dinitrophenylhydrazine (2,4-DNPH).

When 2,4-DNPH is added to a solution of aldehyde or ketone, a **yellow/ orange precipitate** is produced. The formation of this coloured precipitate indicates the presence of a **C=O carbonyl group**.

Distinguishing between aldehydes and ketones

Simple tests can be carried out to detect whether a compound is an aldehyde or a ketone.

Ketones are **not easily oxidised** whereas **aldehydes** are **easily oxidised** to carboxylic acids.

After identifying a solution as a carbonyl using 2,4-DNPH, certain reactions can be carried out using **oxidising agents**. A **positive result** indicates that an **aldehyde** is present while a **negative result** suggests a **ketone** is present.

Acidified potassium dichromate(VI)

Aldehyde - orange solution turns green.

Ketone - no visible change / solution remains orange.

Tollen's reagent

Aldehyde - silver mirror forms on the walls of the test tube.

Ketone - no visible change.

Fehling's reagent

Aldehyde - blue solution gives a brick red precipitate.

Ketone - no visible change / solution remains blue.

Deducing the presence of CH_3CO- group

A CH_3CO- group can be detected using **alkaline aqueous iodine,** I_2.

Iodine is added to the carbonyl, followed by **sodium hydroxide** (to make the solution alkaline). If the CH_3CO- group is present, a **yellow precipitate** of **tri-iodomethane** (CHI_3) will form.

$$CH_3COR + 3I_2 + 4NaOH \rightarrow RCOONa + CHI_3 + 3NaI + 3H_2O$$