



Cambridge (CIE) A Level Chemistry



Aldehydes & Ketones

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Production of Aldehydes & Ketones

- **Aldehydes** and **ketones** are carbonyl compounds containing a C=O group
- They can be prepared from the oxidation of **primary** and **secondary alcohols** respectively

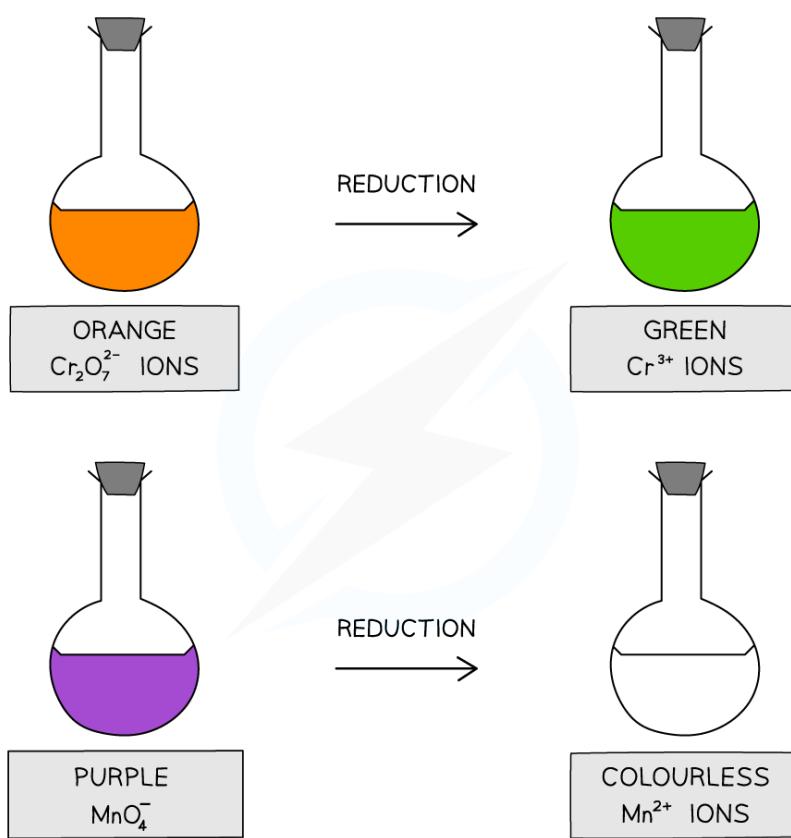
Oxidising agents

- The oxidising agents used to prepare aldehydes and ketones from alcohols include **acidified potassium dichromate** ($K_2Cr_2O_7$) and **acidified potassium manganate** ($KMnO_4$)
- Acidified with dilute sulfuric acid, **potassium dichromate(VI)**, $K_2Cr_2O_7$, is an orange oxidising agent
 - When the alcohols are **oxidised** the orange dichromate ions ($Cr_2O_7^{2-}$) are reduced to green Cr^{3+} ions
- Acidified with dilute sulfuric acid, **potassium manganate(VII)**, $KMnO_4$ is a purple oxidising agent
 - When the alcohols are **oxidised** the purple manganate ions (MnO_4^-) are reduced to colourless Mn^{2+} ions

The colour change in common oxidising agents



Your notes



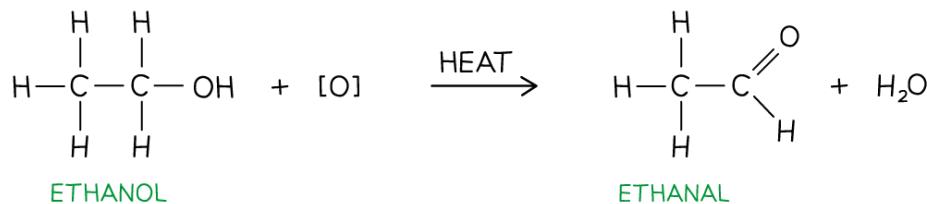
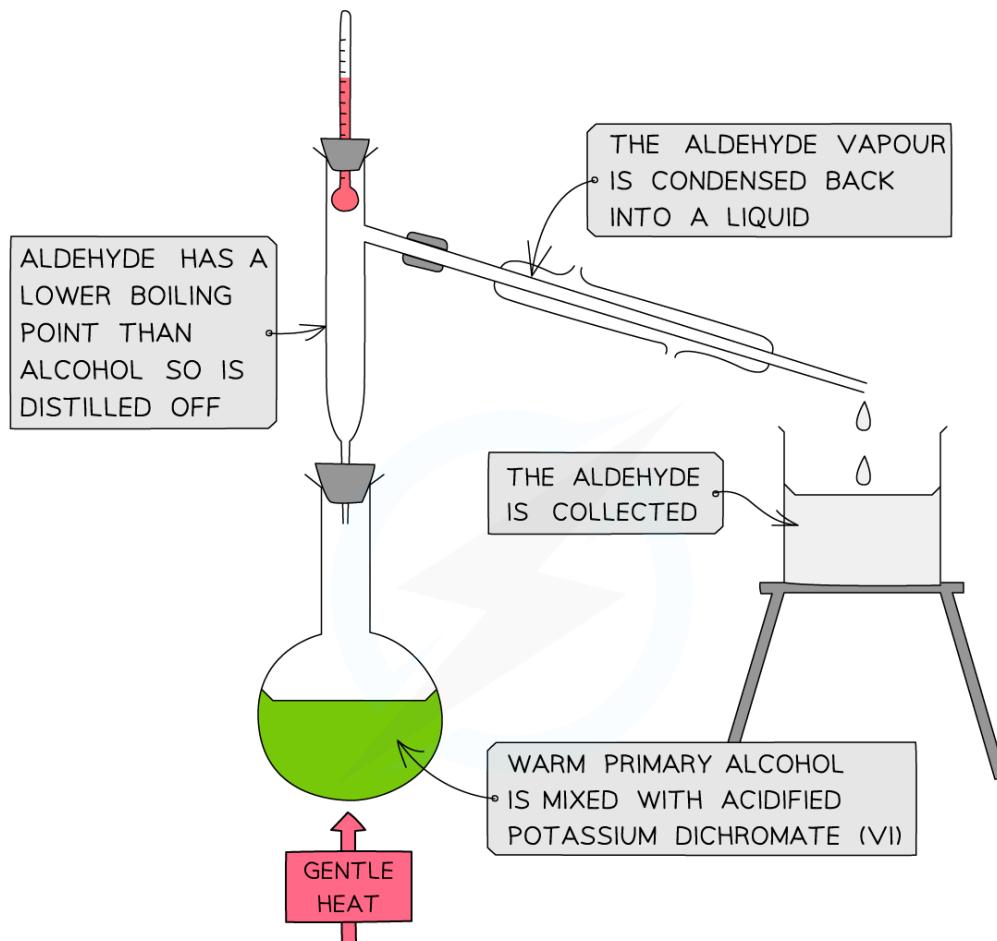
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The oxidising agents change colour when they oxidise an alcohol and get reduced themselves

Synthesis of aldehydes

- To make an aldehyde, **warm primary alcohol** is slowly added to the oxidising agent
- The formed aldehyde has a lower boiling point than the alcohol and can therefore be **distilled off** as soon as it forms
- The aldehyde is then condensed into a liquid and **collected**

Using distillation to oxidise a primary alcohol to an aldehyde



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Aldehydes are formed from the oxidation of primary alcohols

Synthesis of ketones

- To make a ketone, **warm secondary alcohol** is slowly added to the oxidising agent
 - Since the formed **ketone** cannot be further oxidised it does not need to be **distilled off straightaway** after it has been formed

Oxidation of propan-2-ol





Your notes



Examiner Tips and Tricks

If the aldehyde formed is not distilled off, further **refluxing** with excess oxidising agent will oxidise the aldehyde to a **carboxylic acid**

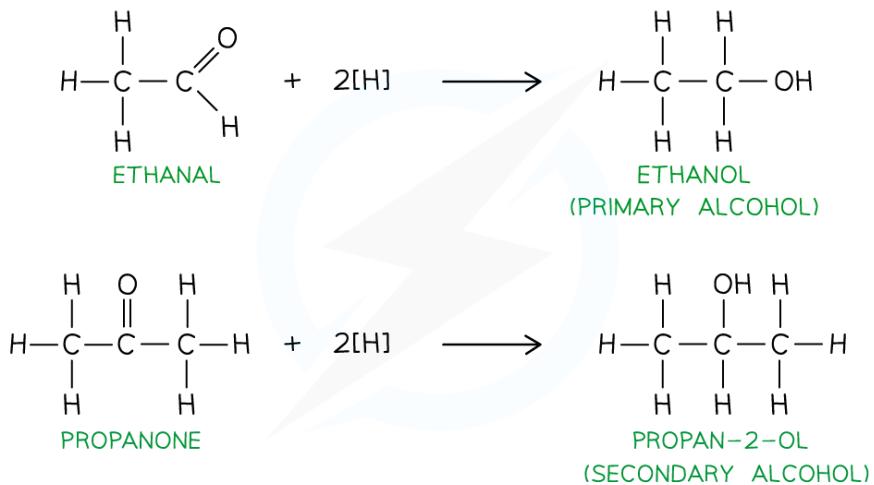


Reactions of Aldehydes & Ketones

Reduction of aldehyde & ketones

- Aldehydes and ketones can be reduced by reducing agents such as NaBH_4 or LiAlH_4
- Aldehydes are reduced to **primary alcohols**
- Ketones are reduced to **secondary alcohols**

Reduction of ethanal and propanone



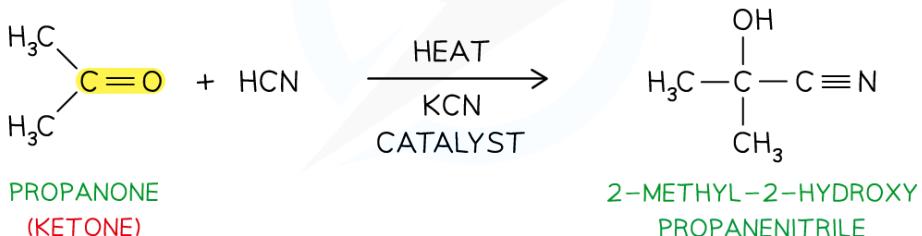
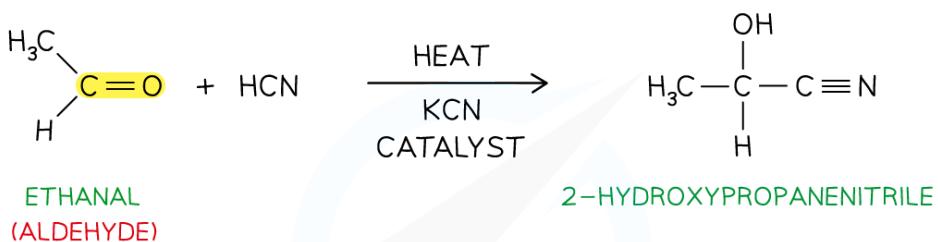
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Aldehydes are reduced to form **primary alcohols**, while ketones are reduced to form **secondary alcohols**

Nucleophilic addition with HCN

- Aldehydes and ketones can undergo **nucleophilic addition** with **hydrogen cyanide**, HCN
- The cyanide ion, CN^- , acts as a nucleophile and adds across the C-O bond
- Aldehydes and ketones react with HCN, KCN as catalyst and heat to produce **hydroxynitriles**
 - Hydroxynitriles are nitriles containing a hydroxy, $-\text{OH}$, group

Nucleophilic addition of HCN to ethanal and propanone


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The nucleophilic addition of HCN to aldehydes always forms a chiral hydroxy nitrile compound, while the nucleophilic addition of HCN to ketones may form a chiral hydroxy nitrile compound



Examiner Tips and Tricks

Catalytic hydrogenation (using $\text{H}_2/\text{Pt}/\text{Ni}$) is indeed a powerful method that **can** reduce aldehydes and ketones to alcohols. However, this reaction often requires different (sometimes harsher) conditions than the hydrogenation of an alkene. This is not in the specification

The nucleophilic addition of HCN to an aldehyde or ketone increases the length of the carbon chain by one carbon atom!



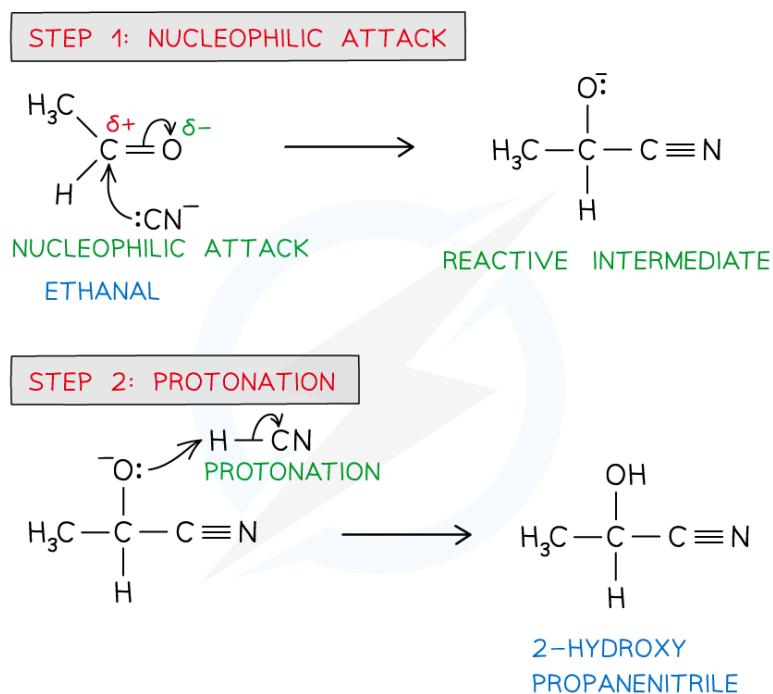
Reaction of Hydrogen Cyanide with Aldehydes & Ketones

- The carbonyl group $-C=O$, in aldehydes and ketones is **polarised**
- The oxygen atom is more **electronegative** than carbon drawing electron density towards itself
- This leaves the carbon atom **slightly positively charged** and the oxygen atom **slightly negatively charged**
- The carbonyl carbon is therefore susceptible to attack by a **nucleophile**, such as the cyanide ion

Nucleophilic addition

- The nucleophilic addition of hydrogen cyanide to carbonyl compounds is a two-step process
- In **step 1** the cyanide ion attacks the carbonyl carbon to form a negatively charged intermediate
- In **step 2** the negatively charged oxygen atom in the reactive intermediate quickly reacts with aqueous H^+ (either from HCN, water or dilute acid) to form 2-hydroxynitrile

The nucleophilic addition of HCN mechanism



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The cyanide ion attacks the carbonyl carbon to form a negatively charged intermediate which quickly reacts with a proton to form a 2-hydroxynitrile compound



Examiner Tips and Tricks

The actual negative charge on the cyanide ion is on the **carbon atom** and not on the **nitrogen atom**



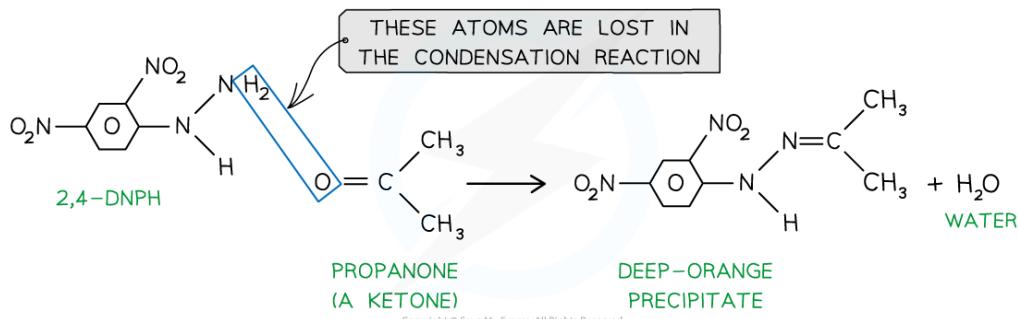
Your notes



Testing for Carbonyls: 2,4-DNPH

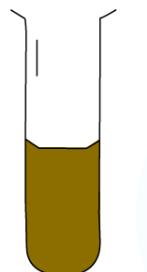
- 2,4-dinitrophenylhydrazine (also known as **2,4-DNPH**) is a reagent which detects the presence of **carbonyl compounds** (compounds with -C=O group)
- The carbonyl group of **aldehydes** and **ketones** undergoes a **condensation** reaction with 2,4-dinitrophenylhydrazine
 - A condensation reaction is a reaction in which two molecules join together and a small molecule (such as H₂O or HCl) is eliminated
- The **product** formed when 2,4-DNPH is added to a solution that contains an aldehyde or ketone is a **deep-orange precipitate** which can be purified by recrystallisation
- The **melting point** of the formed precipitate can then be measured and compared to literature values to find out which specific aldehyde or ketone had reacted with 2,4-DNPH

Example reaction of a ketone with 2,4-DNPH

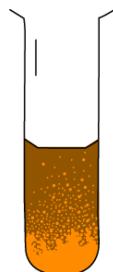


Ketones and aldehydes react with 2,4-DNPH in a condensation reaction

Results of chemical tests using 2,4-DNPH



NEGATIVE TEST WITH 2,4-DNPH
(UNKNOWN SUBSTANCE IS NOT AN ALDEHYDE/KETONE)



POSITIVE TEST WITH 2,4-DNPH
(UNKNOWN SUBSTANCE IS AN ALDEHYDE/KETONE)

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The test tube on the left shows a negative 2,4-DNPH test and the tube on the right shows a positive test



Examiner Tips and Tricks

The 2,4-DNPH is especially useful as other carbonyl compounds such as **carboxylic acids** and **esters** do not give a **positive** test



Your notes

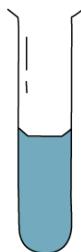
Identifying Carbonyls: Fehling's Solution & Tollens' Reagent

- The presence of an aldehyde group (-CHO) in an **unknown compound** can be determined by the **oxidising agents** Fehling's and Tollens' reagents

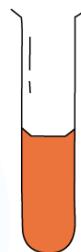
Fehling's solution

- Fehling's solution** is an alkaline solution containing copper(II) ions which act as the oxidising agent
- When **warmed** with an aldehyde, the aldehyde is oxidised to a carboxylic acid and the Cu^{2+} ions are reduced to Cu^+ ions
 - In the alkaline conditions, the carboxylic acid formed will be neutralised to a carboxylate ion (the $-\text{COOH}$ will lose a proton to become $-\text{COO}^-$)
 - The carboxylate ion ($-\text{COO}^-$) will form a salt with a positively charged metal ion such as sodium ($-\text{COO}^-\text{Na}^+$)
- The **clear blue** solution turns **opaque** due to the formation of a **red precipitate**, **copper(I) oxide**
- Ketones** cannot be oxidised and therefore give a **negative test** when warmed with Fehling's solution

Colour change using Fehling's solution



CLEAR BLUE FEHLING'S SOLUTION WITH Cu^{2+} IONS



OPAQUE RED PRECIPITATE OF Cu_2O AS:
– Cu^{2+} IS REDUCED TO Cu^+
– ALDEHYDE IS OXIDISED TO CARBOXYLIC ACID

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The copper(II) ions in Fehling's solution are oxidising agents. They can oxidise an aldehyde to a carboxylic acid and are themselves reduced to copper(I) ions in the copper(I)oxide precipitate

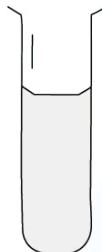
Tollens' reagent



Your notes

- **Tollens' reagent** is an aqueous alkaline solution of silver nitrate in excess ammonia solution
 - Tollens' reagent is also called **ammoniacal silver nitrate solution**
- When **warmed** with an aldehyde, the aldehyde is oxidised to a carboxylic acid and the Ag^+ ions are reduced to Ag atoms
 - In the alkaline conditions, the carboxylic acid will become a carboxylate ion and form a salt
- The Ag atoms form a silver 'mirror' on the inside of the tube
- **Ketones** cannot be oxidised and therefore give a **negative test** when warmed with Tollens' reagent

Colour change using Tollens' reagent



TOLLENS' SOLUTION
WITH Ag^+ IONS



A SILVER 'MIRROR' OF Ag
ATOMS IS FORMED AS:
– Ag^+ IS REDUCED TO Ag
– ALDEHYDE IS OXIDISED
TO CARBOXYLIC ACID

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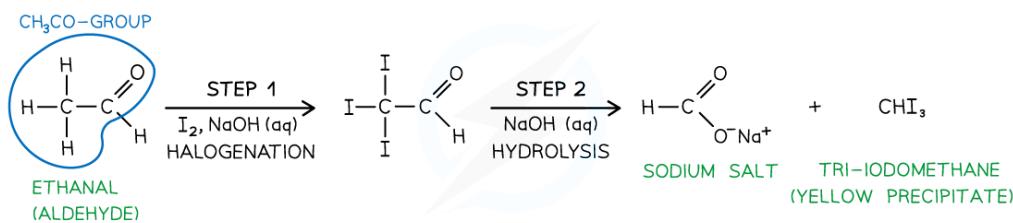
The Ag^+ ions in Tollens' reagent are oxidising agents. They can oxidise an aldehyde to a carboxylic acid and are themselves reduced to silver atoms



Iodoform Reaction

- Tri-iodomethane (also called **iodoform**) is a **yellow precipitate**
- It is formed from the reaction of **iodine** in an alkaline solution with **methyl ketones**
 - Methyl ketones are compounds that have a $\text{CH}_3\text{CO}-$ group
 - **Ethanal** also contains a $\text{CH}_3\text{CO}-$ group and therefore also forms a yellow precipitate with iodoform
- The reagent is **heated** with an **alkaline** solution of **iodine**
- This reaction involves a **halogenation** and **hydrolysis** step
 - In the **halogenation** step, all three H-atoms in the $-\text{CH}_3$ (methyl) group are replaced with iodine atoms, forming a $-\text{Cl}_3$ group
 - The intermediate compound is hydrolysed by an **alkaline** solution to form a sodium salt ($\text{RCO}_2^- \text{Na}^+$) and a yellow precipitate of CHI_3

The iodoform reaction



The reaction of ethanal with iodoform results in the formation of a yellow precipitate