Edexcel International A Level (IAL) Chemistry

Your notes

Organic Chemistry: Carbonyls

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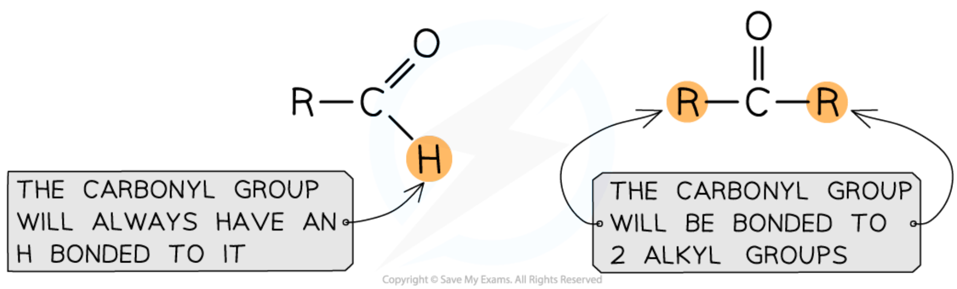
Carbonyls – Aldehydes & Ketones

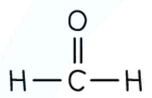
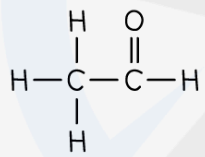
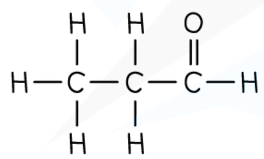
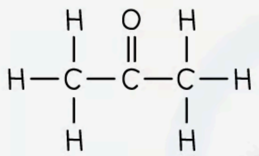
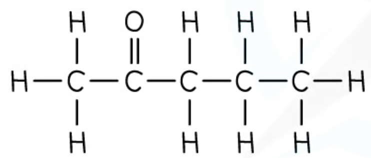
Aldehydes and ketones contain the carbonyl functional group, C=O This is why aldehydes and ketones are also known as carbonyls The difference between aldehydes and ketones is the groups bonded to the carbon of the carbonyl group



- The carbonyl group in an aldehyde is always situated at the end of the chain
  - When naming aldehydes, you do not include the '1' in the name, the carbonyl carbon is always number 1 on the chain
  - The simplest aldehyde is methanal, HCHO, with the only carbon being that of the carbonyl group
- The carbonyl group in a ketone is always situated in the middle of the chain
  - The simplest ketone is propan-2-one, CH_3COCH_3, as you need an alkyl group either side of the carbonyl carbon in a ketone

Aldehyde and Ketone Examples Table

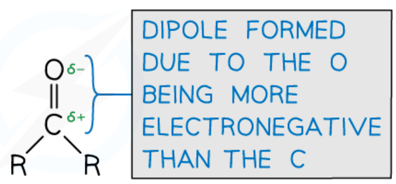
Your notes

Structural Formula	Name	Molecular Formula
	methanal (also known as formaldehyde)	CH_2O
	ethanal	C_2H_4O
	propanal	C_3H_6O
	propanone (also known as acetone)	C_3H_6O
	pentan–2–one	$C_5H_{10}O$

Carbonyls – Hydrogen Bonding

Intermolecular forces of carbonyls

- Aldehydes and ketones have a dipole within their structure due to the electronegative oxygen of the carbonyl group



The carbonyl group has a dipole with a δ+ carbon and a δ– oxygen

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- This means that aldehydes and ketones have permanent dipole-dipole interactions and London forces between molecules
- There are no polar bonds in aldehydes or ketones that can result in a δ+ hydrogen for hydrogen bonding, e.g. O-H, N-H
- Therefore, the melting and boiling points of aldehydes and ketones are lower than their corresponding alcohol

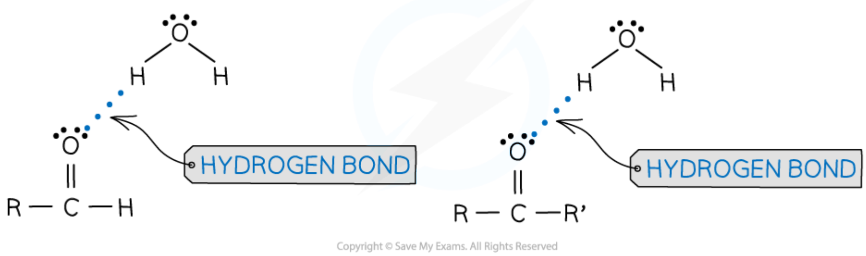
Table comparing boiling points for aldehydes, ketones and their equivalent alcohols

Aldehyde/ketone	Boiling point, C	Equivalent alcohol	Boiling point, C
Methanal	−19	Methanol	65
Ethanal	20	Ethanol	78
Propanal	49	Propan−1−ol	97
Butanal	75	Butan−1−ol	118
Pentanal	103	Pentan−1−ol	138
Propanone	56	Propan−2−ol	83
Butanone	80	Butan−2−ol	100
Pentan−2−one	101	Pentan−2−ol	119
Pentan−3−one	102	Pentan−3−ol	116

Hydrogen bonding

- Although carbonyls cannot hydrogen bond with themselves, they do have the lone pairs on their oxygen
- This means that smaller aldehydes and ketones are able to hydrogen bond with water
    - The δ– oxygen atom from the carbonyl uses its lone pairs to form hydrogen bonds with the δ+ hydrogen from water
- As a result of this hydrogen bonding, smaller aldehydes and ketones will dissolve in water
- Larger aldehydes and ketones have longer hydrocarbon chains which cannot hydrogen bond with water

- These hydrocarbon chains can disrupt the hydrogen bonding within water but cannot form hydrogen bonds themselves
- If a carbonyl compound is large enough, they will not dissolve in water
  - To understand this, you have to consider:
    - The intermolecular forces (London forces) between the carbonyl molecules
    - The hydrogen bonding within water
    - The potential hydrogen bonding of the carbonyl molecule with water
  - In order to dissolve, the strength of the potential hydrogen bonding of the carbonyl with water must be higher than the combined strength of the intermolecular forces of the carbonyl and the hydrogen bonding of water



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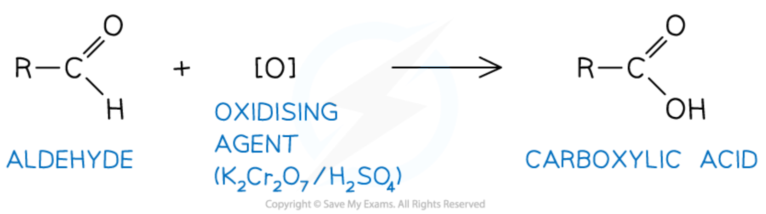
Carbonyls – Reactions

- Carbonyl compounds can undergo a number of reactions, some of which allow you to distinguish between an aldehyde and a ketone
    1. **Oxidation** - with **acidified potassium dichromate(VI)** solution, **Tollens' reagent** or **Fehling's** / Benedict's solution
    2. **Reduction** - with lithium tetrahydridoaluminate / lithium aluminium hydride in dry ether
    3. **Nucleophilic addition** - with HCN or acidified KCN
    4. Non-specific carbonyl testing
        1. **2,4-dinitrophenylhydrazine (2,4-DNPH)** - to identify a carbonyl compound
        2. **Iodoform** test - iodine in the presence of alkali

Acidified potassium dichromate(VI)

- Aldehydes can be oxidised to form carboxylic acids using acidified potassium dichromate(VI) solution
    - $K_2Cr_2O_7$ (aq) with sulfuric acid, H_2SO_4



General reaction of an aldehyde with an oxidising agent

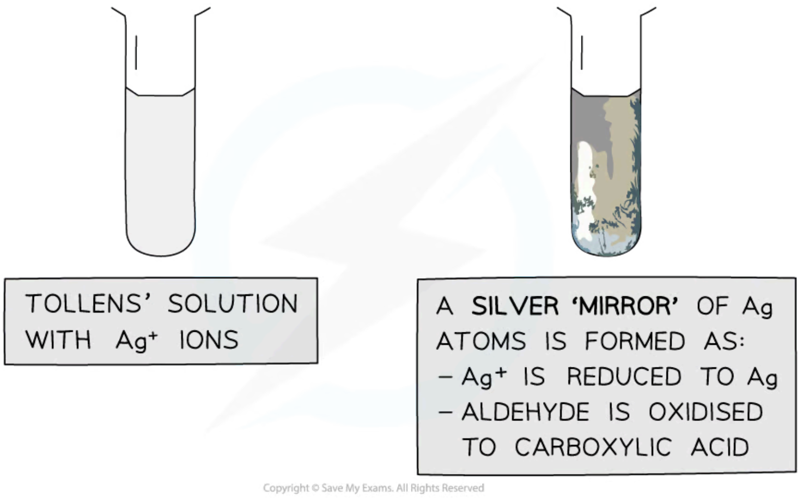
- Ketones are very resistant to being oxidised
    - This is because ketones do not have a readily available hydrogen atom, like aldehydes do
    - An extremely strong oxidising agent would be needed for oxidation of a ketone to take place
    - Such oxidation will likely oxidise a ketone in a destructive way, breaking a C-C bond
- Heating with acidified potassium dichromate can distinguish between an aldehyde and a ketone
    - The aldehyde would be oxidised, and you would see an orange to green colour change
    - The ketone would not be oxidised, so you would see no colour change

Tollens' reagent

- Tollens' reagent contains the silver(I) complex ion $[Ag(NH_3)_2]^+$
- This is formed when aqueous ammonia is added to a solution of silver nitrate
  - Tollens' reagent is also known as ammoniacal silver nitrate
- If gently warmed with Tollens' reagent, an aldehyde will become oxidised
- The silver(I) complex ion solution, $[Ag(NH_3)_2]^+$, is colourless
- As the aldehyde is oxidised, it causes the $[Ag(NH_3)_2]^+$ ions to become reduced to solid metallic silver, Ag
- This is why a positive test result is called a "silver mirror"

Positive Test Result:

- When Tollens' reagent is gently warmed with an aldehyde, the silver mirror is formed
  - This is the positive test result
- When Tollens' reagent is gently warmed with a ketone, no silver mirror will be seen, as the ketone cannot be oxidised by Tollens' reagent, so no reaction takes place
  - This is a negative test result

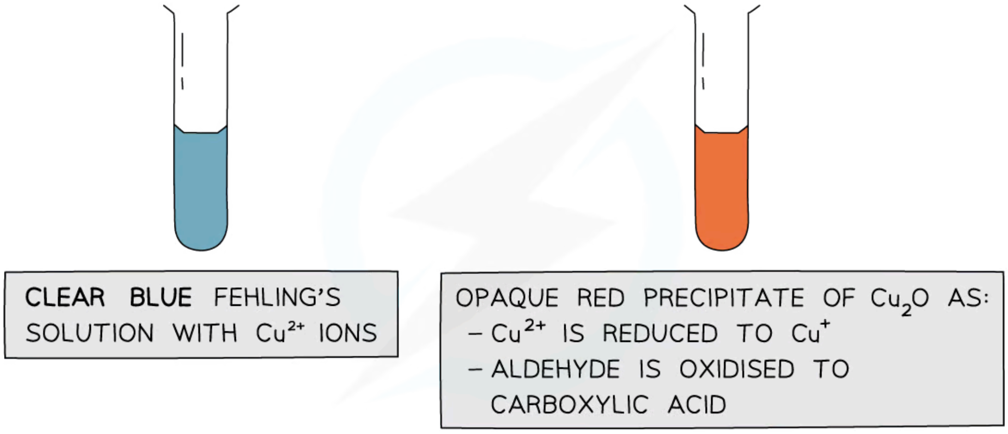


The Ag^+ ions in Tollens' reagent are oxidising agents, oxidising the aldehyde to a carboxylic acid and getting reduced themselves to silver atoms

Fehling's Solution

- Fehling's solution is a solution containing copper(II) ions dissolved in sodium hydroxide, which act as the oxidising agent
  - Benedict's solution is exactly the same as Fehling's solution but the copper(II) ions are dissolved in sodium carbonate

- If an aldehyde is warmed with Fehling's solution, the aldehyde will be oxidised and a colour change will take place
- Fehling's solution is blue, because of the copper(II) complex ions present
- During the reaction, as the aldehyde is oxidised to a carboxylic acid, the blue Cu^{2+} ions are reduced to Cu^{+} ions and a brick red precipitate is formed
- The brick red precipitate is copper(I) oxide
- If a ketone is warmed with Fehling's solution, no reaction takes place as the ketone will not be oxidised, so the solution will remain blue



The copper(II) ions in Fehling's solution are oxidising agents, oxidising the aldehyde to a carboxylic acid and getting reduced themselves to copper(I) ions in the Cu_2O precipitate

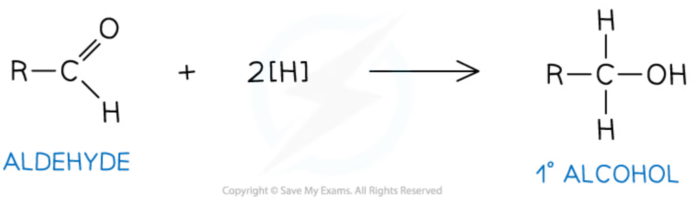
Examiner Tips and Tricks

You are expected to know all of the above methods which can be used to distinguish between an aldehyde and a ketone! However, Tollens' reagent is the most commonly used method, if trying to identify an unknown sample for example.

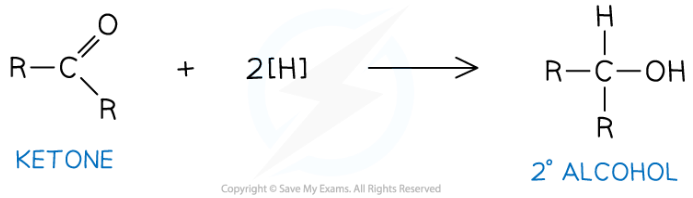
Reduction of Carbonyls

- Aldehydes are reduced to primary alcohols and ketones are reduced to secondary alcohols
- This is done with lithium tetrahydridoaluminate / lithium aluminium hydride, $LiAlH_4$, in dry ether
  - The $LiAlH_4$ generates a hydride ion nucleophile, $:H^-$
  - The hydride ion reduces the carbonyl group in an aldehyde or a ketone
    - When this reaction takes place, it is an example of a nucleophilic addition reaction

Your notes



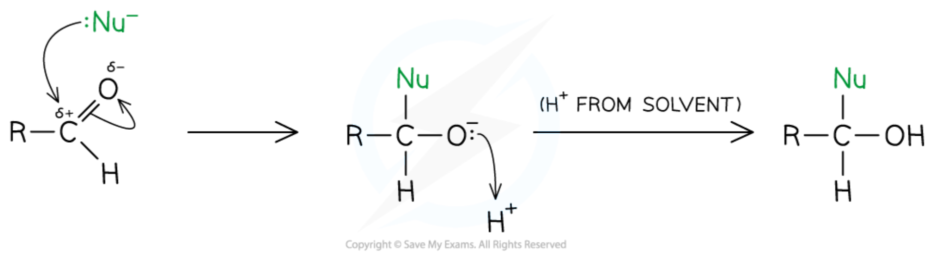
Reduction equation for an aldehyde



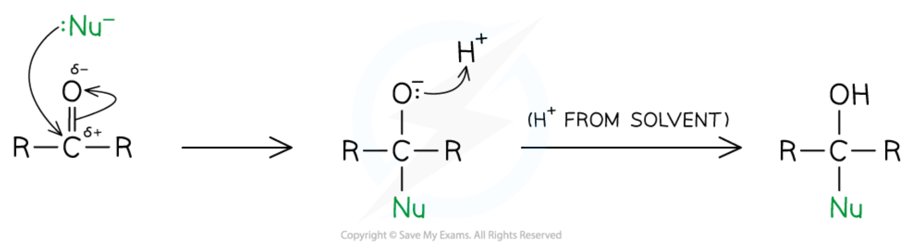
Reduction equation for a ketone

Nucleophilic addition

- Many of the reactions which carbonyl compounds undergo are nucleophilic addition reactions
- 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



General Mechanism with an aldehyde

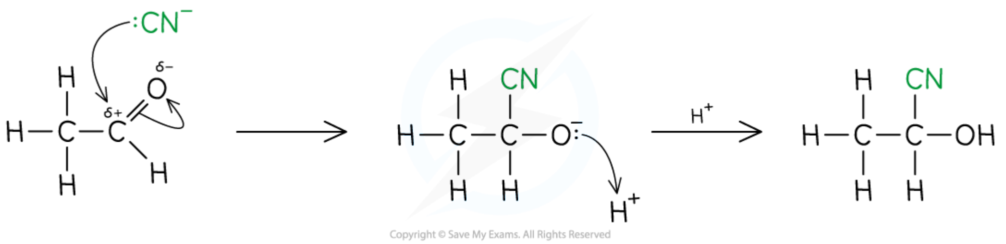


General Mechanism with a ketone

- In both reactions, the nucleophile (Nu) attacks the carbonyl carbon to form a negatively charged intermediate which quickly reacts with a proton

Addition of HCN to carbonyl compounds

The nucleophilic addition of hydrogen cyanide to carbonyl compounds is a two-step process, as shown below



- 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 compounds,
  - e.g. 2-hydroxypropanenitrile
- This reaction is important in organic synthesis, because it adds a carbon atom to the chain, increasing the chain length
- The products of the reaction are hydroxynitriles
  - The nitrile group is the priority functional group so it is attached to carbon 1 and results in the suffix -nitrile
  - The hydroxyl group is not the priority functional group so the hydroxyl group is named using the hydroxy- prefix, rather than the -ol suffix

2,4-dinitrophenylhydrazine (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

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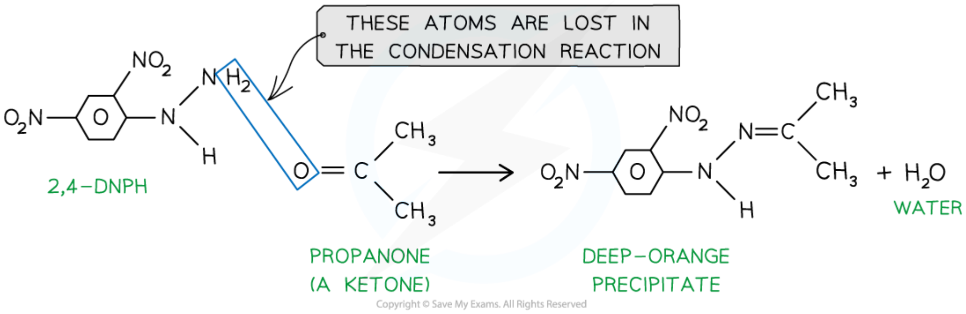
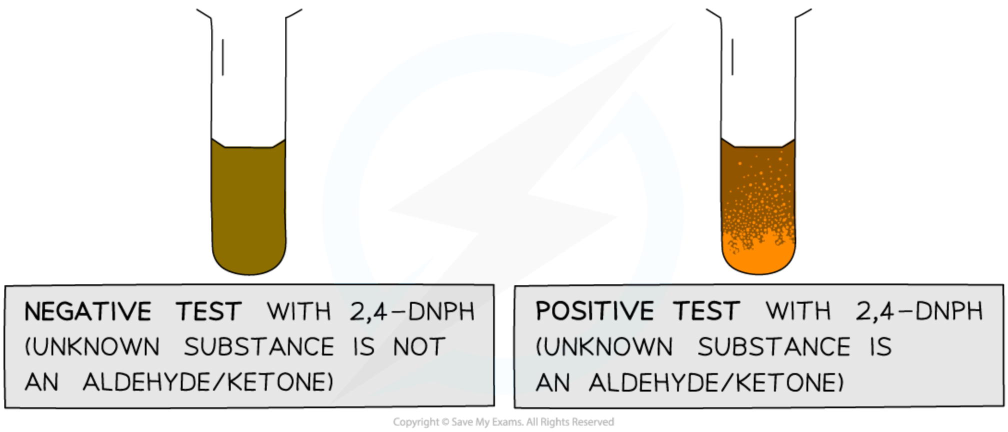
- A condensation reaction is a reaction in which two molecules join together and a small molecule (such as H_2O or HCl) is eliminated

- 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



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



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 test is especially useful as other carbonyl compounds such as carboxylic acids and esters do not give a positive result

Iodoform test

- **Tri-iodomethane** (also called **iodoform**) forms a **yellow precipitate** with **methyl ketones**

- Methyl ketones are compounds that have a CH_3CO-group
- **Ethanal** also contains a CH_3CO- 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 -CH_3 (methyl) group are replaced with iodine atoms, forming a -CI_3 group
  - The intermediate compound is hydrolysed by an **alkaline** solution to form a sodium salt (RCO_2^- Na^+) and a yellow precipitate of CHI_3

The reaction of ethanal with iodoform results in the formation of a yellow CHI_3 precipitate

- The overall reaction equation is

$CH_3COCH_3 + 3I_2 + 4OH^- \rightarrow CH_3COO^- + CHI_3 + 3I^- + 3H_2O$

Alcohols and the iodoform test

- If an alcohol contains a R-CH(OH)-CH_3 group it will also produce a yellow precipitate in this test
  - These include all methyl secondary alcohols (such as hexan-2–ol) and the primary alcohol ethanol
- Iodine in sodium hydroxide reacts to form iodate(I) ions which will oxidise the secondary alcohols to ketones

Iodination of carbonyls under acidic conditions

- If propanone is treated with iodine solution under acid conditions a different reaction takes place
- A hydrogen atom in propanone is replaced by an iodine atom, producing iodopropanone

$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$

- The iodopropanone is colourless and forms slowly
- This makes this a very useful reaction to study kinetics as the yellow-brown colour of the iodine fades so it is an ideal reaction to monitor using colorimetry

Your notes

- By varying the concentrations of propanone, iodine and hydrogen ions you can easily determine the reaction orders and overall rate equation

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