

CHAPTER 18: Carbonyl Compounds

18.1 Introduction to Aldehydes and Ketones

18.2 Reactions Aldehydes and Ketones

18.3 Tests for Aldehydes and Ketones

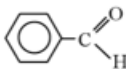
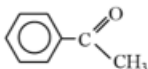
Learning outcomes:

- (a) describe:
 - (i) the formation of aldehydes and ketones from primary and secondary alcohols respectively using $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$.
 - (ii) the reduction of aldehydes and ketones, e.g. using NaBH_4 or LiAlH_4 .
 - (iii) the reaction of aldehydes and ketones with HCN and NaCN .
- (b) describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones.
- (c) describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) reagent to detect the presence of carbonyl compounds.
- (d) deduce the nature (aldehyde or ketone) of an unknown carbonyl compound from the results of simple tests (i.e. Fehling's and Tollens' reagents; ease of oxidation).

18.1 Introduction to Aldehydes and Ketones

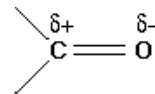
What are carbonyl compounds?

- 1) Carbonyl compounds are compounds that contain the C=O(carbonyl) group. Examples are aldehydes and ketones.

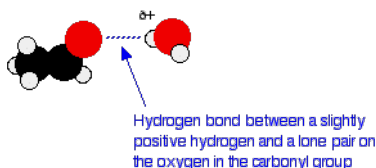
<i>Aldehydes</i>	<i>Ketones</i>
<p>➤ C=O group at the <i>end of a carbon chain</i>.</p> <p>➤ at least one H atom attached to the carbonyl C atom.</p> <p style="text-align: center;">$R-C(=O)H$</p> <p>e.g.</p> <div style="display: flex; justify-content: space-around;"> <div> $H-C(=O)H$ methanal </div> <div> $CH_3-C(=O)H$ ethanal </div> <div> $CH_3CH_2-C(=O)H$ propanal </div> <div>  benzaldehyde </div> </div>	<p>➤ C=O group <i>in the carbon chain</i>.</p> <p>➤ two alkyl or aryl groups attached to the carbonyl C atom.</p> <p style="text-align: center;">$R-C(=O)R'$</p> <p>e.g.</p> <div style="display: flex; justify-content: space-around;"> <div> $CH_3CH_2-C(=O)CH_3$ propanone </div> <div> $CH_3CH_2CH_2-C(=O)CH_3$ butanone </div> <div> $CH_3CH_2CH_2CH_2-C(=O)CH_3$ pentan-3-one </div> <div>  phenylethanone </div> </div>

Physical properties of carbonyl compounds

- 1) i. The boiling point of carbonyl compounds is higher than the alkanes with similar M_r .
- ii. The boiling point increases with increasing number of carbon atom. This is because there are more electrons, hence more temporary dipoles can be set up. More energy is required to overcome these forces.
- ii. Besides temporary dipoles, permanent dipole-dipole forces are also present due to carbonyl compounds being polar.
- iii. Methanal and ethanal are gases at room temperature, while others are liquids.



- 2) i. Carbonyl compounds are soluble in water. This is because they are able to form hydrogen bond with water molecules.



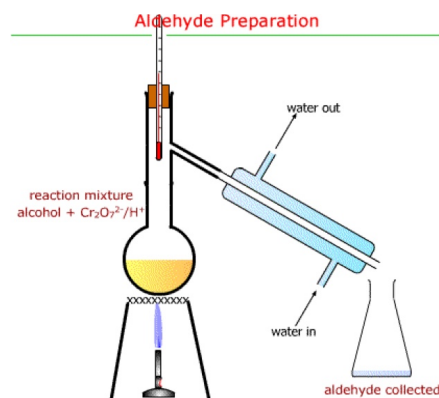
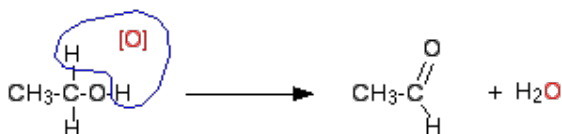
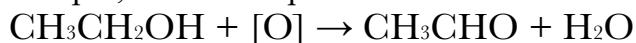
- ii. The solubility decreases with increasing number of carbon atoms. This is because the long hydrocarbon chain disrupts the hydrogen bonding.

Preparation of aldehydes and ketones

1) Aldehydes and ketones can be made by **oxidising primary and secondary alcohol respectively**. The oxidising agent used is either acidified potassium dichromate(VI), $\text{K}_2\text{Cr}_2\text{O}_7$ or acidified potassium manganate(VII), KMnO_4 .

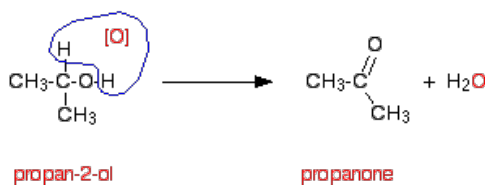
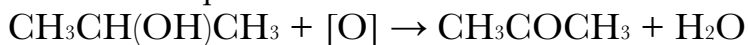
2) To make an **aldehyde**:

- The primary alcohol used must be in excess and heated under reflux with acidified $\text{K}_2\text{Cr}_2\text{O}_7/\text{KMnO}_4$. The aldehyde formed **must be distilled off as soon as possible**.
- Under these conditions, a primary alcohol is oxidised to an aldehyde. Take ethanol as an example, ethanal is produced.



3) To make a **ketone**:

- The secondary alcohol is heated under reflux with acidified $\text{K}_2\text{Cr}_2\text{O}_7/\text{KMnO}_4$.
- Under these conditions, a secondary alcohol is oxidised to a ketone. Take propan-2-ol as an example:



18.2 Reactions of Aldehydes and Ketones

Reactivity of carbonyl compounds

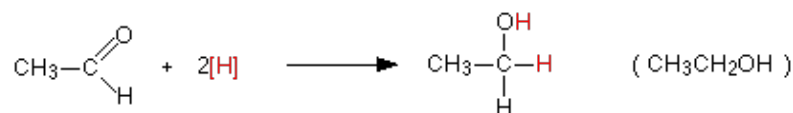
- 1) The C=O bond of the carbonyl group is highly polarised due to oxygen atom being more electronegative.
- 2) This causes the slightly positive carbon atom to be susceptible to nucleophilic attacks. Nucleophiles are something that carries a negative charge.
- 3) Therefore, carbonyl compounds will undergo **nucleophilic addition**.
- 4) Summary of reactions carbonyl compounds undergo:
 - i. Reduction.
 - ii. Oxidation.
 - iii. Reaction with hydrogen cyanide, HCN.

Reduction

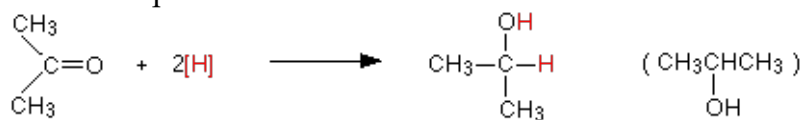
- 1) **Reagent** : Lithium tetrahydridoaluminate, LiAlH_4 or sodium tetrahydridoborate, NaBH_4
Condition : For LiAlH_4 - in dry ether
 For NaBH_4 - in aqueous alcoholic solution
Product : Aldehyde - primary alcohol
 Ketone - secondary alcohol
- 2) LiAlH_4 and NaBH_4 are acting as reducing agents as well as providing the nucleophile, H^- . This is a redox reaction as well as a nucleophilic addition reaction.



- 3) For aldehydes, **primary alcohols** are formed upon reduction. Take ethanal as an example:



- 4) For ketones, **secondary alcohols** are formed upon reduction. Take propanone as an example:



5) Note:

- i. Due to the reactivity of LiAlH_4 , it cannot be used in the presence of water or alcohol. It must be carried out in solution in a carefully dried ether such as ethoxyethane(diethyl ether).

Oxidation

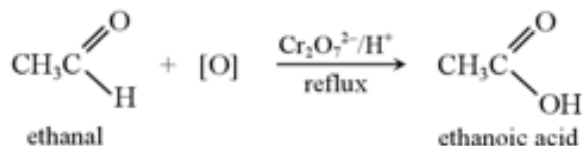
- 1) **Reagent** : Acidified potassium dichromate(VI), $\text{K}_2\text{Cr}_2\text{O}_7$ or acidified potassium manganate(VI), KMnO_4

Condition : Heat under reflux

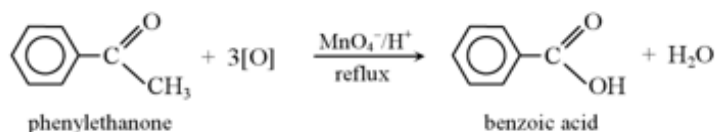
Product : Aldehyde - Carboxylic acid

Ketone - Will not be oxidised.

- 2) Aldehydes will be oxidised to **carboxylic acids**. Take ethanal as an example:



- 3) Ketones **will not be oxidised** by acidified $\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4 . The only exception is phenylethanone.



Reaction with hydrogen cyanide, HCN

- 1) **Reagent** : Sodium/potassium cyanide, NaCN and a little sulfuric acid, H_2SO_4

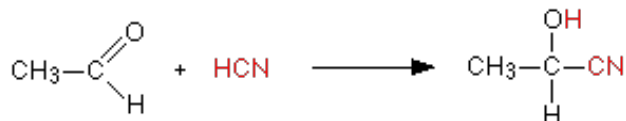
Condition : Room temperature

Product : Hydroxynitriles

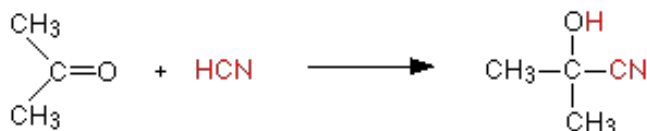
2) Hydrogen cyanide is not used alone because it is a poisonous gas. Instead, it is produced from the reaction between sodium/potassium cyanide and sulfuric acid. The solution will contain hydrogen cyanide and some free cyanide ions.

3) For both aldehydes and ketones, **hydroxynitriles** are produced.

i. For aldehydes, take ethanal as an example, 2-hydroxypropanenitrile is produced.



ii. For ketones, take propanone as an example, 2-hydroxy-2-methylpropanenitrile is produced.

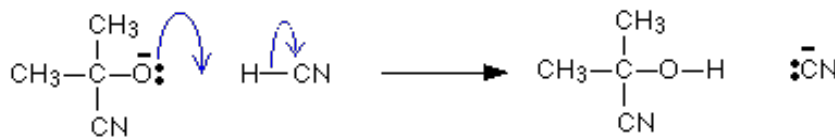


4) The mechanism of this reaction - **nucleophilic addition**:

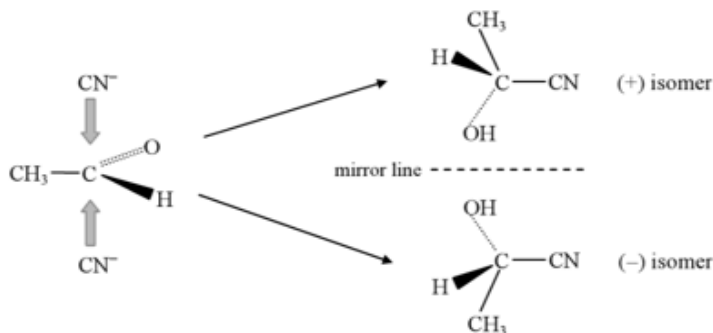
i. The electron-deficient carbon atom is attacked by the nucleophile, CN^- .



ii. The negative ion formed then picks up a hydrogen ion from hydrogen cyanide, or from the water



5) Such a reaction will produce a mixture of different isomers. This is because carbonyl compounds are planar and the cyanide ion has equal chance of attacking from above or below the plane of the molecule.



18.3 Tests for Aldehydes and Ketones

Test for carbonyl group using 2,4-dinitrophenylhydrazine(2,4-DNPH)

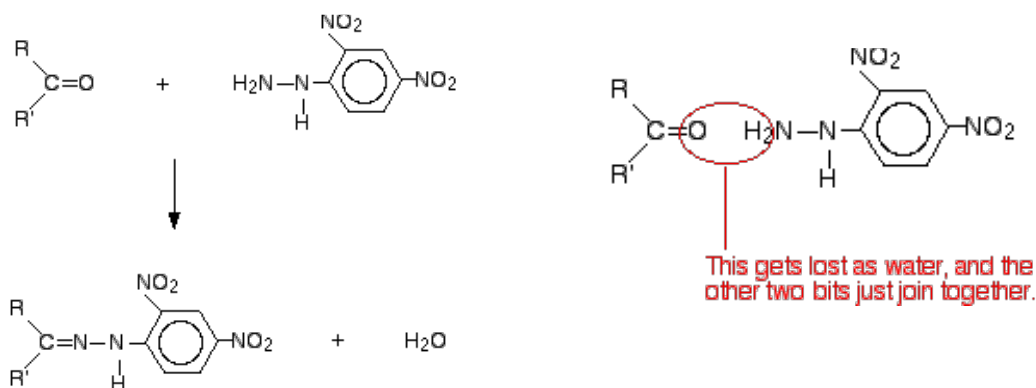
- 1) 2,4-dinitrophenylhydrazine or 2,4-DNPH can be used **to detect the presence of carbonyl group, C=O**. The structure of 2,4-DNPH is shown below:



- 2) This test is usually carried out using Brady's reagent, that is, a solution of the 2,4-dinitrophenylhydrazine in methanol and sulfuric acid.
- 3) When a little aldehyde or ketone is added to the Brady's reagent, an **orange-yellow precipitate** is formed.



- 4) A **condensation reaction** occurs when a carbonyl compound is added to 2,4-DNPH. During this reaction, a water molecule is lost. The final compound is seen as orange-yellow precipitate.



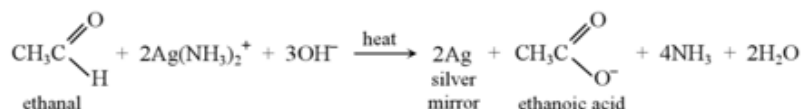
Test for aldehydes using Tollens' reagent(silver mirror test)

- 1) Tollens' reagent contains **diamminesilver(I) ions, $[\text{Ag}(\text{NH}_3)_2]^+$** . Aldehydes will reduce the diamminesilver(I) ions to metallic silver, aldehyde itself is oxidised to a salt of carboxylic acid.
- 2) Since ketones will not be oxidised, it will not reduce it to metallic silver.

- 3) Therefore, when a few drops of aldehyde is added to the freshly prepared Tollens' reagent, and warmed in a water bath for a few minutes, **a grey precipitate or a silver mirror** is observed only if aldehyde is present.




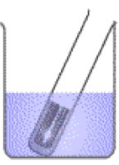


- 4) Take ethanal as an example, the equation is:



- 5) The details on the preparation of Tollens' reagent are as shown below.

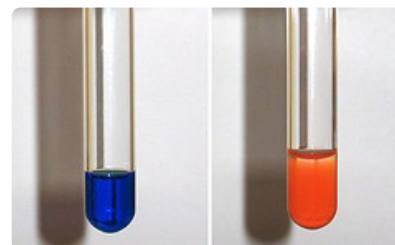
Tollens' reagent test for aldehydes

<p>Step 1 Prepare a solution of silver nitrate</p> 	<p>Step 2 Add sodium hydroxide solution dropwise until no further reaction. A light brown precipitate forms</p> 
<p>Step 3 Add concentrated ammonia solution dropwise until the brown ppt of Ag₂O just redissolves. The silver ions have been complexed into [Ag(NH₃)₂]⁺ ions.</p> 	<p>Step 4 Add a few drops of the suspected aldehyde and stand the solution in a warm water bath. If a silver mirror forms after a few minutes then the test is positive.</p> 

Aldehydes are reducing agents and can reduce silver(I) to elemental silver. Ketones cannot. In the process the aldehyde itself gets oxidised to a carboxylic acid.

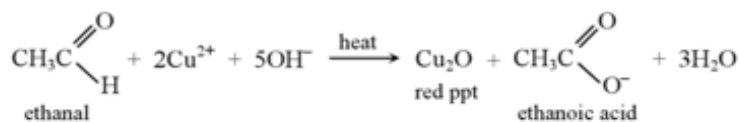
Test for aldehydes using Fehling's solution

- 1) Fehling's solution contains **copper(II) ions complexed with tartrate ions** in sodium hydroxide solution. Complexing the copper(II) ions with tartrate ions prevents precipitation of copper(II) hydroxide. It is a blue solution.
- 2) Only aldehydes will reduce the complexed copper(II) ion to copper(I) oxide. Because the solution is alkaline, the aldehyde itself is oxidised to a salt of the corresponding carboxylic acid.



3) When a few drops of the aldehyde is added to the reagent, and the mixture is warmed gently in a hot water bath for a few minutes, a **red precipitate** is observed only if aldehydes present.

4) Take ethanal as an example, the equation is:



Summary

Comparing aldehydes and ketones:

	<i>Ethanal, CH₃CHO</i>	<i>Propanone, CH₃COCH₃</i>
Reduction: LiAlH ₄ (in dry ether)	primary alcohol formed. product: ethanol, CH ₃ CH ₂ OH	secondary alcohol formed. product: CH ₃ CH(OH)CH ₃
HCN (step-up reaction)	hydroxynitrile formed. product: CH ₃ CH(OH)CN	hydroxynitrile formed. product: (CH ₃) ₂ C(OH)CN
2,4-DNPH (test for carbonyl)	orange ppt. formed.	orange ppt. formed.
Iodoform test: aq. I ₂ + aq. NaOH	yellow crystals of CHI ₃ formed.	yellow crystals of CHI ₃ formed.
Oxidation: Cr ₂ O ₇ ²⁻ /H ⁺ (reflux)	carboxylic acid formed. orange Cr ₂ O ₇ ²⁻ turns green. product: ethanoic acid	—
<i>Fehling's Solution</i>	red ppt. (Cu ₂ O) formed. (no reaction with benzaldehyde)	—
<i>Tollens' Reagent</i>	grey ppt. (or silver mirror) formed.	—

Note: Sodium boron hydride, NaBH₄ (in methanol), may also be used to reduce a carbonyl group.