

Lecture Notes 15 Carbonyl Compounds



Lecturer: Ms Theresia Line Ishak

Content

- Aldehydes (exemplified by ethanal)
 - (i) oxidation to carboxylic acid
 - (ii) nucleophilic addition with hydrogen cyanide
 - (iii) characteristic tests for aldehydes
- Ketones (exemplified by propanone and phenylethanone)
 - (i) nucleophilic addition with hydrogen cyanide
 - (ii) characteristic tests for ketones

Learning Outcomes

Candidates should be able to:

- (a) describe the formation of aldehydes and ketones from, and their reduction to, primary and secondary alcohols respectively
- (b) describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones
- (c) explain the differences in reactivity between carbonyl compounds and alkenes towards nucleophilic reagents, such as lithium aluminium hydride and hydrogen cyanide
- (d) describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) to detect the presence of carbonyl compounds
- (e) 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)
- (f) describe the presence of a CH₃CO– group in a carbonyl compound from its reaction with alkaline aqueous iodine to form tri-iodomethane

Reference texts

- 1. Understanding Chemistry for Advanced level, Ted Lester, Janet Renshaw
- 2. Chemistry for Advanced Level. Peter Cann, Peter Hughes
- 3. Organic Chemistry, John McMurry

JC2/2025

1 Introduction

Carbonyl compounds contain the **carbonyl group (C=O)**. They are further classified into **Aldehydes** and **Ketones**.



2 Nomenclature

Aldehyde		Ketone		
Name	Name Structural Formula		Structural Formula	
Methanal		Propanone	СН ₃ СОСН ₃ 0 H ₃ C СН ₃	
Ethanal	CH₃CHO O II H ^C CH₃	Pentan-2-one	$CH_{3}COCH_{2}CH_{2}CH_{3}$	
Cyclohexanecarbaldehyde		Cyclohexanone	 o	
Phenylethanal	C ₆ H ₅ CH ₂ CHO	Phenylethanone	C ₆ H ₅ COCH ₃ O II C CH ₃	
Benzaldehyde	C ₆ H ₅ CHO			

3 Structure of the carbonyl functional group

 The carbonyl carbon atom is sp² hybridised and joined to three other atoms by forming σ bonds. The carbonyl carbon atom and the three atoms bonded to it form a trigonal planar structure with bond angle of 120°.



Orbitals of the carbonyl carbon

The **unhybridised 2p orbital** of the carbonyl carbon overlaps side-on with a 2p orbital of the oxygen atom to form a π **bond**.



• As the oxygen atom is more **electronegative** compared to the carbon atom, it causes the carbonyl carbon to be electron deficient. Hence it carries a slight positive charge (δ +) while the oxygen atom carries a slight negative charge (δ -).



The electron deficient carbon is thus susceptible to attack by nucleophiles like CN⁻.

Difference in reactivity between Carbonyl compounds and Alkenes

- Although both alkenes (C=C) and carbonyl compounds (C=O) are unsaturated with double bonds, they **behave differently towards nucleophilic reagents**.
- **Carbonyl carbon is electron-deficient** since it is bonded to electronegative oxygen. The electronegative oxygen pulls electrons from the carbonyl carbon, causing the carbonyl carbon to be electron deficient and attracts nucleophiles.
- On the other hand, there is no electronegativity difference between the two C atoms in the C=C bond, hence the bond is non-polar and there is **no electron deficient carbon** for the nucleophile to attack. In addition, the π bond causes the C=C bond to be electron-rich, repelling the approach of a nucleophile.



4 Physical properties

4.1 Boiling Point

• Carbonyl compounds are polar in nature. They have stronger intermolecular **permanent dipole – permanent dipole** attraction which cause them to have higher boiling point than alkanes and other non-polar compounds of comparable relative molecular mass, M_r.

compounds	M,	boiling point / °C
CH ₃ CH ₂ CH ₂ CH ₃	58.0	- 0.5
CH ₃ CH ₂ CHO	58.0	48
CH ₃ COCH ₃	58.0	56

• However they **do not exhibit hydrogen bonding** between molecules as there is no H attached to an electronegative atom like N, O, or F. Hence they have lower boiling points than alcohols and carboxylic acids of comparable relative molecular mass, M_r.

compounds	Mr	boiling point / °C
CH ₃ CH ₂ CHO	58.0	48
CH ₃ CH ₂ CH ₂ OH	60.0	97
CH₃COOH	60.0	118

• The order of boiling points for compounds with **comparable M**_r but different functional group is:

carboxylic acids	>	alcohols	>	aldehydes/ketones	>	alkanes
------------------	---	----------	---	-------------------	---	---------

Carboxylic acids	Alcohol	Aldehydes/Ketones	Alkanes
Hydrogen bonding exists between molecules.		Permanent dipole – permanent dipole attraction exist between molecules.	Weak instantaneous dipole – induced dipole attraction exist between molecules.

4.2 Solubility

• The **lower aliphatic** aldehydes and ketones (i.e. the carbonyl group is not attached to the benzene ring) are appreciably soluble in water due largely to their ability to form **hydrogen bonds** with water molecules. (Note that carbonyl compounds are however unable to form hydrogen bonding between themselves!)



• Higher members containing more than 5 carbons and the aromatic substituents are virtually **insoluble** in water.

As the chain length increases, the carbonyl molecule becomes **largely non-polar**. **Instantaneous dipole – induced dipole attraction** between the hydrocarbon chains in the carbonyl molecules become more significant. The energy evolved from the formation of instantaneous dipole – induced dipole attraction between water and carbonyl molecules is **insufficient** to overcome the instantaneous dipole – induced dipole – induced dipole – induced dipole attraction between carbonyl molecules and hydrogen bonding between water molecules.

Overview of carbonyl reactions

OXIDATION





5 Preparation of Aldehydes and Ketones

5.1 Controlled oxidation of primary alcohols by acidified potassium dichromate(VI) give aldehydes

Oxidation
$K_2Cr_2O_7$, $H_2SO_4(aq)$, heat with immediate distillation
To convert primary alcohols to aldehydes
$\begin{array}{c} H \\ H - C \\ R \\ R \\ primary alcohol \end{array} + \begin{bmatrix} 0 \\ - \end{array} R - C \\ H \\ aldehyde \end{array} + H_2 O$
Orange K ₂ Cr ₂ O ₇ solution turns green
$\begin{array}{c} H\\ H-C\\ -O-H\\ H\\ methanol \end{array} \stackrel{O}{\longrightarrow} H-C\\ H\\ methanal \end{array} \stackrel{O}{\longrightarrow} H \stackrel{H}{\longrightarrow} H_2O\\ H\\ methanol \end{array} \stackrel{methanal}{\longrightarrow} H \stackrel{H}{\longrightarrow} H_2O\\ H\\ M\\ methanol \end{array} \stackrel{M}{\longrightarrow} H_2O\\ H\\ M\\ M\\$
intermediate aldehyde before they are further oxidised by the KMnO ₄ either to give CO_2 (in the case of methanol) or a carboxylic acid.



5.2 Oxidation of secondary alcohols give ketones

Type of reaction	Oxidation
Reagents and Conditions	 (i) K₂Cr₂O₇, H₂SO₄(aq), heat under reflux OR (ii) KMnO₄, H₂SO₄(aq), heat under reflux
Purpose	To convert secondary alcohols to ketones
Equation	$H \xrightarrow{OH}_{R} R + [O] \longrightarrow O \xrightarrow{O}_{R} R + H_2O$ R secondary alcohol ketone
Observation	 (i) Orange K₂Cr₂O₇ solution turns green (ii) Purple KMnO₄ decolourises
Remarks	$\begin{array}{c} \begin{array}{c} \begin{array}{c} OH\\ H\overset{O}{C}-CH_3 \ + \ [O] \end{array} \longrightarrow \overset{O}{H_3C} -CH_3 \ + \ H_2O \\ \\ \begin{array}{c} Propan-2-ol \end{array} & \begin{array}{c} Propanone \end{array} \end{array}$ Oxidation number of alcoholic carbon in propan-2-ol = 0 + (-1) + (+1) + 0 = 0 \\ \\ \begin{array}{c} Oxidation \ number \ of \ carbonyl \ carbon \ in \ propanone = 0 + (+2) + 0 = +2 \end{array} There is an increase in oxidation number of carbon from 0 in propan-2-ol to +2 in \ propanone \ hence \ an \ oxidation \ has \ occurred \ when \ converting \ propan-2-ol \ to \ propanone. \end{array}

5.3 Oxidation of disubstituted alkenes give ketones

Type of reaction	Oxidation
Reagents and Conditions	KMnO ₄ , H ₂ SO ₄ (aq), heat under reflux
Purpose	To convert alkenes to ketones
Equation	$\begin{array}{c cccc} H_{3}C & CH_{3} \\ H_{3}C & CH_{3} \end{array} + 2[O] \longrightarrow 2 \begin{array}{c} O \\ H_{3}C & CH_{3} \end{array}$
Observation	Purple KMnO ₄ decolourises
Remarks	Aldehydes cannot be obtained from this reaction as they are further oxidised to carboxylic acids readily.

Example

(a) Write a balanced equation for the reaction when hot acidified potassium manganate (VII) is added to propan-2-ol.

$$H \xrightarrow{O}_{C} C \xrightarrow{O}_{C} C \xrightarrow{O}_{H_3} + [O] \longrightarrow \xrightarrow{O}_{H_3} C \xrightarrow{O}_{H_3} C$$

(b) Write a balanced equation for the reaction when acidified potassium dichromate (VI) and ethanol are heated with immediate distillation.

$$H \stackrel{OH}{\longrightarrow} C \stackrel{C}{\longrightarrow} CH_3 + [O] \longrightarrow H \stackrel{O}{\longrightarrow} C \stackrel{OH}{\longrightarrow} CH_3 + H_2O$$

6 Reactions of Aldehydes and Ketones

6.1 Redox reactions of carbonyl compounds

6.1.1 Reduction of aldehydes give primary alcohols

Type of reaction	Reduction
Reagents and Conditions	 (i) LiA/H₄ in dry ether, room temperature OR (ii) NaBH₄, room temperature OR (iii) H₂(g), Ni catalyst, heat OR H₂(g), Pt catalyst, room temperature OR H₂(g), Pd catalyst, room temperature
Purpose	To convert aldehydes back to primary alcohols
Equation	$\begin{array}{c} O\\ CH_3-\overset{H}{C}-H + 2[H] \longrightarrow CH_3-CH_2-OH\\ O\\ CH_3-\overset{H}{C}-H + H_2 \longrightarrow CH_3-CH_2-OH \end{array}$

6.1.2 Reduction of ketones give secondary alcohols

Type of reaction	Reduction
Reagents and Conditions	 (i) LiA/H₄ in dry ether, room temperature OR (ii) NaBH₄, room temperature OR (iii) H₂(g), Ni catalyst, heat OR H₂(g), Pt catalyst, room temperature OR H₂(g), Pd catalyst, room temperature
Purpose	To convert ketones to secondary alcohols
Equation	$\begin{array}{c} O \\ H_{3}C - C - CH_{3} \\ H_{3}C - C - CH_{3} \end{array} + 2[H] \longrightarrow CH_{3} - C - CH_{3} \\ H \\ H_{3}C - C - CH_{3} \\ H_{2} \end{array} \rightarrow CH_{3} - C - CH_{3} \\ H \end{array}$

Oxidation of aldehydes give carboxylic acids

Type of reaction	Oxidation
Reagents and Conditions	 (i) K₂Cr₂O₇, H₂SO₄(aq), heat under reflux OR (ii) KMnO₄, H₂SO₄(aq), heat under reflux
Purpose	To convert aldehydes to carboxylic acids
Equation	$CH_3 - C \xrightarrow{H} H = [O] \longrightarrow CH_3 - C \xrightarrow{H} O OH$
Observation	 (i) Orange K₂Cr₂O₇ solution turns green (ii) Purple KMnO₄ decolourises
Remarks	Ketones cannot be further oxidised. Hence acidified K ₂ Cr ₂ O ₇ and KMnO ₄ solution can be used to distinguish between aldehydes and ketones. Watch YouTube clip:

Summary of redox reactions



Example

(a) Give the structural formula of the organic product formed when the following compound



reacts with



(b) Write a balanced equation for the reaction in (a)(i).



Note: Use [H] when balancing equation using NaBH₄

6.2 Reaction with HCN (hydrogen cyanide)

Type of reaction	Nucleophilic addition
Reagents and Conditions	 (i) HCN in the presence of a trace amount of NaOH(aq), 10–20 °C OR (ii) HCN in the presence of a trace amount of NaCN(aq), 10–20 °C
Purpose	To form the cyanohydrin product (a cyano and a hydroxy group are attached to the same carbon atom) To lengthen the carbon chain length by one carbon (step up reaction) and introducing an –OH group attached to the original carbonyl carbon
Equation	(1) $CH_3 - C - H + HCN \longrightarrow CH_3 - C - H - H - CN - CN - CN - CN - CN - $
Remarks	 Recall: 1. Chain lengthening via nucleophilic substitution by heating halogenoalkane with ethanolic NaCN under reflux. CH₃CH₂X + NaCN (alc) <u>heat under</u> > CH₃CH₂CN + NaX 2. Nitriles can undergo a. acidic hydrolysis to give carboxylic acid heating under reflux with mineral acid e.g. HC/(aq), H₂SO₄(aq) b. reduction to give primary amine using any of the following: LiA/H₄ in dry ether H₂ with Pt / Pd catalyst, room temp / H₂ with Ni catalyst and heat

Example

Write balanced equations when (a) ethanal and (b) propanone react with DCN in a trace amount of base under cool temperature conditions.

(D represents Deuterium, an isotope of the hydrogen atom)

(a)



(b)



Example

Complete the following:



Summary of common reducing agents and their uses

Reducing agent	Condition	Functional group	Equation		
LiA/H₄ dry ether		Nitriles Aldehydes Ketones Carboxylic acids Esters Amides	CH ₃ CN + 4[H] → CH ₃ CH ₂ NH ₂ CH ₃ CHO + 2[H] → CH ₃ CH ₂ OH CH ₃ COCH ₃ + 2[H] → (CH ₃) ₂ CH(OH) CH ₃ COOH + 4[H] → CH ₃ CH ₂ OH + H ₂ O CH ₃ COOCH ₃ + 4[H] → CH ₃ CH ₂ OH + CH ₃ OH CH ₃ CONHCH ₃ + 4[H] → CH ₃ CH ₂ NHCH ₃ + H ₂ O		
NaBH₄	-	Aldehydes Ketones	CH ₃ CHO + 2[H] → CH ₃ CH ₂ OH CH ₃ COCH ₃ + 2[H] → (CH ₃) ₂ CH(OH)		
H₂	Ni, heat/ Pt or Pd, room temperature	Alkenes Nitriles Aldehydes Ketones Nitrobenzene	$CH_{2}=CH_{2} + H_{2} \rightarrow CH_{3}CH_{3}$ $CH_{3}CN + 2H_{2} \rightarrow CH_{3}CH_{2}NH_{2}$ $CH_{3}CHO + H_{2} \rightarrow CH_{3}CH_{2}OH$ $CH_{3}COCH_{3} + H_{2} \rightarrow (CH_{3})_{2}CH(OH)$ $\qquad \qquad $		
Sn, conc HC/ (Zn, Fe may be used) followed by NaOH(aq) Nitrobenzene (N		Nitrobenzene	1. Sn, conc HC/ $NO_2 + 6[H] NH_2 + 2H_2O$ NH_3^+ forms after reaction with Sn, conc HC/. NaOH is then added to liberate the)		

6.2.1 Nucleophilic Addition Mechanism

Type of reaction: Nucleophilic Addition

Mechanism	Description (not required in answers)
N≡C—H + NaOH \longrightarrow Na ⁺ + NC [•] + H ₂ O	Step 1: Generation of the nucleophile, CN ⁻ HCN is a weak acid and only slightly ionised in aqueous solutions. Hence trace amount of strong base is added to help generate the nucleophile CN ⁻ . If the reagent is HCN with a trace amount of NaOH, then the first step will be: HCN + NaOH → Na ⁺ + CN ⁻ + H ₂ O If the reagent is HCN with a trace amount of NaCN, then the first step will be: NaCN → Na ⁺ + CN ⁻
$NC^{\stackrel{{}{}} \xrightarrow{H_3C} \xrightarrow{\delta^+} \xrightarrow{\delta^-} \xrightarrow{slow}} H \xrightarrow{CH_3} H \xrightarrow{CH_3} O^-$ $H \xrightarrow{C} \xrightarrow{C} \xrightarrow{C} \xrightarrow{O} \xrightarrow{C} \xrightarrow{Slow} H \xrightarrow{C} \xrightarrow{C} \xrightarrow{C} \xrightarrow{O} \xrightarrow{C} \xrightarrow{C} \xrightarrow{O} \xrightarrow{C} \xrightarrow{C} \xrightarrow{O} \xrightarrow{C} \xrightarrow{O} \xrightarrow{C} \xrightarrow{O} \xrightarrow{O} \xrightarrow{C} \xrightarrow{O} \xrightarrow{O} \xrightarrow{O} \xrightarrow{O} \xrightarrow{O} \xrightarrow{O} \xrightarrow{O} O$	 Step 2: Nucleophilic attack CN⁻ nucleophile attacks and is added to the electron deficient carbonyl carbon (which has a partial positive charge) to form the negatively charged tetrahedral intermediate. Note the change in hybridisation of the carbonyl carbon from sp² to sp³ and the change in bond angle around the carbonyl carbon from 120° to 109°
H - C - O = + H + C - C + A + C + C + C + A + C + C + C + C +	Step 3: Formation of cyanohydrin product and regeneration of CN ⁻ The negatively charged tetrahedral intermediate reacts with the HCN molecule to form the cyanohydrin product and regenerate the nucleophile CN ⁻ . Note: Overall, the HCN is essentially added across the C=O double bond.

6.2.2 Optical activity of cyanohydrin product

Recall in **Step 2** of the nucleophilic addition mechanism, the nucleophile attacks the **electron deficient carbonyl carbon**.

Step 2:



trigonal planar carbonyl compound

chiral centre present in this intermediate

The CN⁻ nucleophile can attack the **trigonal planar carbonyl carbon** of the molecule from **either the top or bottom of the plane** with **equal probability**, producing **equal amounts of each enantiomer** (a racemic mixture).



The product mixture is **optically inactive** (i.e. does not rotate plane-polarised light) as **each enantiomer rotate plane-polarised light in the opposite direction by the same magnitude** hence the **rotating powers of the enantiomers cancel out**.

Note:

- Use of unsymmetrical carbonyl compounds are required to give a chiral product.
- While chiral products are formed, no optical activity is observed as a racemic mixture is obtained.



6.2.3 Reactivity of Aldehydes and Ketones

Ketones are **generally less reactive** than aldehydes towards nucleophiles. This is because:

- the carbonyl carbon in ketone is **less electron-deficient** than aldehyde as it is attached to two electron-donating alkyl groups. Hence, ketones are less susceptible to nucleophilic attack.
- the carbonyl carbon in ketone is attached to two bulky alkyl groups hence it is **more sterically hindered**, preventing nucleophiles from attacking the carbonyl carbon.

6.3 Reaction of carbonyl compounds with 2,4-dinitrophenylhydrazine (2,4-DNPH)

Type of reaction	Condensation		
Reagents and Conditions	2,4-dinitrophenylhydrazine (2,4-DNPH), warm		
Equation	$\begin{array}{c} R \\ R $		
Observation	Orange ppt (2,4-dinitrophenylhydrazone) formed		
Remarks	This is a useful chemical test to detect the presence of aldehydes or ketones .		

Example

Write a balanced equation for the reaction between (a) ethanal, and (b) propanone with 2,4-DNPH respectively.



6.4 Tri-iodomethane (lodoform) test

Type of reaction	Oxidation				
Reagents and Conditions	I₂(aq), NaOH(aq), warm				
Equation	$ \begin{array}{c} O \\ II \\ C \\ C \\ CH_3 \end{array} + 3I_2 + 4NaOH \xrightarrow{warm} CHI_3 + O \\ Vellow \\ ppt \end{array} + R^{-C} O^{-}Na^{+} + 3NaI + 3H_2O $				
Observation	Yellow ppt of tri-iodomethane, CHI ₃ (s) formed (antiseptic smell)				
	Used to test for the presence of $CH_3 - C - R$ or $CH_3 - C - R$ groups of OH				
	Recall OH $R-C-CH_3 + 4I_2 + 6NaOH \xrightarrow{warm} CHI_3 + R^{O}_{II} + C^{O}_{II} + 5NaI + 5H_2O$ H H				
	If the alkali is not specified, write an ionic equation instead.				
Remarks	$ \begin{array}{c} O \\ II \\ R^{-}C \\ CH_{3} \end{array} + 3I_{2} + 4OH^{-} \xrightarrow{warm} CHI_{3} + O \\ yellow \\ ppt \end{array} + R^{-}C \\ O^{-} + 3I^{-} + 3H_{2}O \\ O^{-} \end{array} $				
	Steps involved in oxidative cleavage (not required by syllabus but can be tested as an application question): 1. Substitution of the hydrogens to form tri-iodoketone				
	$R \xrightarrow{O} CH_{3} \xrightarrow{O} R \xrightarrow{O} CH_{2}I \xrightarrow{O} R \xrightarrow{O} CHI_{2} \xrightarrow{O} R \xrightarrow{O} CHI_{2}$				
	2. Attack by the OH ⁻ causing the C–C bond to break				
	$R - C - CI_3 + OH^- \rightarrow R - C - O^- + CHI_3$				

Example

Put a tick if the following compounds give yellow precipitate with aqueous alkaline iodine.



Example

Which of the following compounds will give a positive tri-iodomethane test? If there is any reaction, write a balanced equation for the reaction.

(a) butanone (b) butan-2-ol

(a)
$$\begin{array}{c} O \\ CH_{3}CH_{2}-C-CH_{3}+3I_{2}+4NaOH \longrightarrow CHI_{3}+CH_{3}CH_{2}-C-O^{-}Na^{+}+3NaI+3H_{2}O \\ \end{array}$$
(b)
$$\begin{array}{c} O \\ CH_{3}-C-H+4I_{2}+6NaOH \longrightarrow CHI_{3}+CH_{3}CH_{2}-C-O^{-}Na^{+}+5NaI+5H_{2}O \\ CH_{2}CH_{3} \end{array}$$

6.5 Chemical tests to distinguish between aldehydes and ketones

Fehling's reagent or Tollens' reagent can be used to **distinguish aldehydes from ketones**.

6.5.1 Reaction of aldehydes with Fehling's reagent

Type of reaction	Oxidation				
Reagents and Conditions	Fehling's reagent (a mixture of Cu²+/NaOH(aq)), warm				
Equation	RCHO + $2Cu^{2+}$ + $5OH^{-}$ \longrightarrow RCO_2^{-} + Cu_2O + $3H_2O$				
Observation	Brick-red ppt of Cu(I) oxide, Cu ₂ O is produced if aldehyde is present. Watch YouTube clip:				
	This test is used to distinguish between aldehydes and ketones. Ketones will not produce the brick-red ppt because ketones cannot be further oxidised , i.e. it cannot reduce Cu ²⁺ to Cu ₂ O.				
	Note: Benzaldehyde does not react with Fehling's reagent even though it is an aldehyde				
Remarks	 Not in syllabus Unlike aliphatic aldehydes, they undergo Cannizzaro's reaction (an organic disproportionation reaction) under the influence of sodium hydroxide present in Fehling's reagent. 				
	$2 \bigcirc H + NaOH \longrightarrow O & OH \\ C & O^{-}Na^{+} + OH $				
	 Since the Cu²⁺ is not reduced to Cu₂O, there will be no brick-red ppt observed. 				
	Hence, Fehling's reagent can be used as a chemical test to distinguish between aliphatic and aromatic aldehydes .				

6.5.2 Reaction of aldehydes with Tollens' reagent

Type of reaction	Oxidation
Reagents and Conditions	Tollens' reagent (solution of [Ag(NH ₃) ₂] ⁺ complex), warm
Equation	RCHO + $2Ag^+$ + $3OH^- \xrightarrow{\text{warm}} RCO_2^-$ + $2Ag$ + $2H_2O$
	A shiny silver mirror is formed if aldehyde (aliphatic or aromatic) is present (usually produced on surface of the test tube).
	Watch YouTube clip:
Observation	
	• Tollens' reagent is a stronger oxidising agent than Fehling's reagent. Hence all aldehydes , including benzaldehyde , reacts with Tollens' reagent to produce a silver mirror.
Remarks	• Since ketones cannot be further oxidised, it will not react with Tollens' reagent to produce the silver mirror.
	\therefore this test is used to distinguish between aldehydes and ketones.

In summary,

	Aldehyde	Ketone	Benzaldehyde
Fehling's reagent	\checkmark	х	х
Tollens' reagent	\checkmark	Х	\checkmark

Example

Suggest a simple chemical test to distinguish between propanal and propanone. Write equations for any reactions that occur.

Test: Add Tollens' reagent and warm.

Observation: Propanal: a silver mirror is formed.

 $CH_{3}CH_{2}CHO + 2Ag^{+} + 3OH^{-} \longrightarrow CH_{3}CH_{2}CO_{2}^{-} + 2Ag + 2H_{2}O$

Propanone: no silver mirror formed.

Appendix Mechanism for reaction of a carbonyl compound with 2,4–DNPH

• The hydrazine acts as a nucleophile by attacking the electron deficient carbonyl carbon.



• Proton transfer from nitrogen atom to oxygen atom.



• Elimination of water molecule by removing OH from the carbon atom and H from the adjacent nitrogen atom, forming a C=N bond.



Mechanism for Tri-iodomethane Test

• The hydroxide ion acts as a nucleophile by abstracting the partial positive hydrogen atom to give an enolate. The enolate will then attack the iodine to give the first iodinated product.



• These two steps are repeated to give the second and third iodination products.



• Finally, the hydroxide ion will attack the partial positive carbonyl carbon atom to give a carboxylic acid and ⁻CI₃ ion. The ⁻CI₃ ion will then abstract the acidic proton from the carboxylic acid to give a carboxylate and tri-iodomethane, CHI₃.



Keto-Enol Tautomerism



- The two tautomers, ketone and enol, are isomers, and tautomerism is an equilibrium process.
- Tautomerism arises because of the proximity of an acidic hydrogen to a lone pair of electrons on the carbonyl oxygen atom. The enol is known as such because it contains both the alkene and hydroxy groups.
- The presence of the alkene group makes the enol susceptible to oxidative cleavage.
- As the concentration of enol is insignificant, the position of equilibrium will lie more to the left. Hence, oxidation of ketone is not very prominent.
- However, in the presence of a stronger oxidising agent, the position of equilibrium will lie more to the right, causing enol to be oxidised.