**VICTORIA JUNIOR COLLEGE**
**CHEMISTRY DEPARTMENT**

# JC2 H2 CHEMISTRY
# Carbonyl Compounds (Aldehydes & Ketones)

## LECTURE OUTLINE

| **Lesson** | 1 | 2 |
|---|---|---|
| **Pages** | 1 – 9 | 10 – 14 |
| **Complete by** | 23 Feb | 23 Feb |

**1.** Introduction

**2.** Physical Properties
- **2.1** Boiling point
- **2.2** Solubility in water

**3.** Laboratory Preparation
- **3.1** Oxidation of alcohols

**4.** Reactions
- **4.1** Reactions of the carbonyl group
  - **4.1.1** Nucleophilic addition reaction of HCN
    - **4.1.1.1** Reactions involving cyanohydrin
  - **4.1.2** Condensation reactions
- **4.2** Reduction of aldehydes or ketones
- **4.3** Oxidation of aldehydes
  - **4.3.1** With acidified $K_2Cr_2O_7$ or $KMnO_4$
  - **4.3.2** With Tollens' reagent
  - **4.3.3** With Fehling's solution
- **4.4** Tri-iodomethane formation

https://for.edu.sg/chem2025carbonyls

*scan this QR code to ask questions related to the lecture*

## 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 $LiAlH_4$ and HCN

**(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)** deduce the presence of a $CH_3CO-$ group in a carbonyl compound from its reaction with alkaline aqueous iodine to form tri-iodomethane

## 1 Introduction (Nomenclature/Structure)

- General formula of $C_nH_{2n}O$
- Functional group is C=O
- Include both **(i)** aldehydes, RCHO *(where R = H, alkyl or aryl groups)*
  and **(ii)** ketones, RCOR' *(where R, R' = alkyl or aryl groups)*


aldehyde


ketone

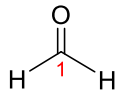
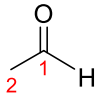
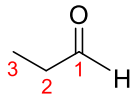
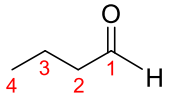
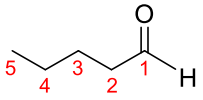
- Carbonyl compounds are widely used in perfume industry (e.g. aliphatic aldehydes with 8 –13 carbon atoms have very pleasant floral odours and are used in feminine perfumery)
- **Nomenclature**

a) **Aldehyde**

for linear chains containing only aldehyde functional group

**1.** count the number of carbon atoms in the chain

**2.** the *'e'* of the *–ane* of the alkane with the same number of carbon atoms is replaced by *'al'*. Note that it is not required to number the position of the aldehyde as it is assigned position 1 within the chain.

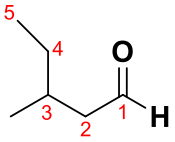
| name | structural formula | skeletal formula |
|---|---|---|
| methanal | HCHO |  |
| ethanal | $CH_3CHO$ |  |
| propanal | $CH_3CH_2CHO$ |  |
| butanal | $CH_3CH_2CH_2CHO$ |  |
| pentanal | $CH_3CH_2CH_2CH_2CHO$ |  |

for branched chains or chains containing substituents (-OH, $-NH_2$, -R (alkyl), -X (halide))

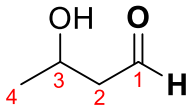
**1.** find the longest alkyl chain, which is the parent chain, that contains the aldehyde group

**2.** assign the aldehyde carbon as carbon position 1 and name the parent chain

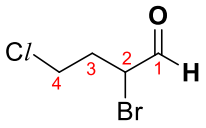
**3.** identify substituent(s) on the parent chain and include its position as prefixes to the name of the parent chain




3-methylpentanal




*3-hydroxybutanal*



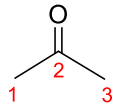
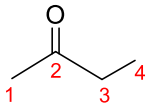
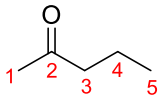
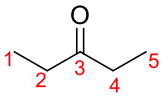

*2-bromo-4-chlorobutanal*

b) **Ketone**

<u>for linear chains containing only ketone functional group</u>

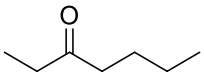
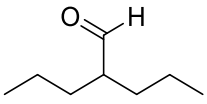
**1.** count the number of carbon atoms in the chain

**2.** the *'e'* of the *–ane* of the alkane with the same number of carbon atoms is replaced by *'one'*. Ketones containing more than 4 carbon atoms can exist as constitutional isomers, so the position of the carbonyl groups need to be specified in the name.

| name | structural formula | skeletal formula |
|---|---|---|
| propanone | $CH_3COCH_3$ |  |
| butanone | $CH_3COCH_2CH_3$ |  |
| pentan-2-one | $CH_3COCH_2CH_2CH_3$ |  |
| pentan-3-one | $CH_3CH_2COCH_2CH_3$ |  |

**Worked Example 1**

Classify the following carbonyl compounds as aldehyde or ketone.
Hence name the compounds.

| | | | |
|---|---|---|---|
| **structure** |  |  | $CH_3CHCICH_2CHO$ |
| **type of carbonyl** | | | |
| **name of compound** | | | |

## 2 Physical Properties

### 2.1 Boiling point

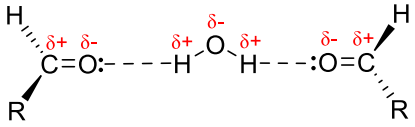
- Carbonyls are **moderately *polar*** because of permanent δ+ charge on the carbonyl C atom and the δ– charge on the O atom of the C=O functional group. (*recall that oxygen is more electronegative than carbon)*
- Hence they have *higher boiling point* than alkanes with similar number of electrons but *lower boiling point* than alcohols with similar number of electrons (comparable $M_r$).

| ***compound*** | ***$M_r$*** | ***b.p. / °C*** | ***dominant intermolecular forces*** |
|---|---|---|---|
| $CH_3CH_2CH_3$ | 44 | – 42 | instantaneous dipole-induced dipole interactions |
| $CH_3CHO$ | 44 | 21 | permanent dipole-permanent dipole interactions |
| $CH_3CH_2OH$ | 46 | 78 | hydrogen bonding |

*Recall that for compounds with similar $M_r$, more energy is required to overcome stronger intermolecular hydrogen bonds than permanent dipole-permanent dipole interactions!*

### 2.2 Solubility in water

- Both ketones and aldehydes are *soluble* in water as they are *polar* and are able to form *hydrogen bonding* with water molecules.
- Both can dissolve *polar* and *non-polar* solutes.




intermolecular **hydrogen bonding** between water and aldehyde molecule

- Solubility in $H_2O$ *decreases* as $M_r$ increases because as the carbon chain increases, the extent of intermolecular hydrogen bonding between the carbonyl compounds and water (solvent-solute interaction) decreases. Thus, less energy is released which makes it more difficult to overcome the hydrogen bonding between water molecules (solvent-solvent interaction).

## 3 Laboratory Preparation

Students should be able to

*a) describe the formation of aldehydes and ketones from, and their reduction to, primary and secondary alcohols respectively*

### 3.1 Oxidation of alcohols

- primary (1°) alcohols $\xrightarrow{\text{oxidation}}$ aldehydes
- secondary (2°) alcohols $\xrightarrow{\text{oxidation}}$ ketones

**<u>Oxidation of primary alcohols (1°)</u>** to prepare **<u>aldehydes</u>**

Reagents and conditions: **$K_2Cr_2O_7$(aq), $H_2SO_4$(aq), heat with immediate distillation**

$$\mathbf{RCH_2OH + [O] \longrightarrow RCHO + H_2O}$$

**Making thinking visible**

**Why is immediate distillation of aldehyde necessary?**

If the aldehyde is not distilled immediately, further heating with acidified dichromate will oxidise the aldehyde to a carboxylic acid. *(oxidation of alcohol to carboxylic acid will be covered in the topic of carboxylic acids and derivatives)*

**Why is distillation of aldehyde possible in a mixture of the alcohol and aldehyde product?**

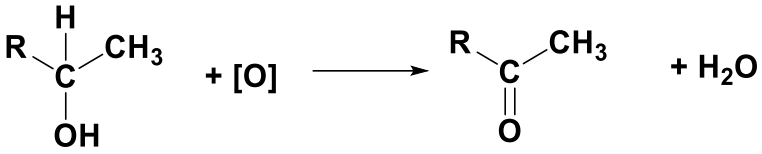
The aldehyde product will always have a lower boiling point than its corresponding alcohol and hence will be boiled off and collected first in the distillation setup.

**Why is $KMnO_4$(aq) not used to oxidise primary alcohol to aldehyde?**

$KMnO_4$(aq) is a very strong oxidising agent that will readily oxidise the aldehyde further to carboxylic acid.

**Oxidation of secondary alcohols (2°)** to prepare **ketones**

Reagents and conditions: **$K_2Cr_2O_7$(aq), $H_2SO_4$(aq), heat**
or **$KMnO_4$(aq), $H_2SO_4$(aq), heat**



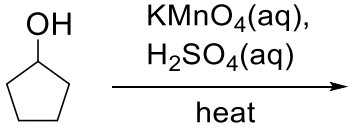

**Making thinking visible**

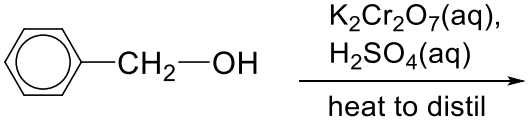
**Why is immediate distillation of ketone not necessary?**

Ketone cannot be further oxidised even with further heating under reflux. Therefore, ketone does not need to be distilled immediately.

**Worked Example 2**

Write down the observations of the following reactions and draw the structures of the organic products.



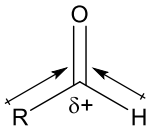



# 4 Reactions

## 4.1 Reactions of the carbonyl group

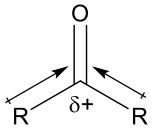
- Ketones are generally **less reactive** than aldehydes towards nucleophiles for two reasons:

  **(i) electronic factor***:* carbonyl carbon of ketone is less electron-deficient as it is attached to two electron-donating alkyl groups




aldehyde

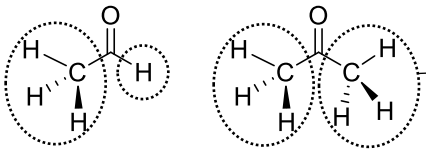
has **only one** electron-donating alky group that stabilises the partial positve charge




ketone

has **two** electron-donating alkyl groups that stabilise the partial positive charge

  **(ii) steric hindrance***:* alkyl group is bulkier than hydrogen. This hinders the approach of the nucleophile to the electron-deficient carbon in carbonyl.



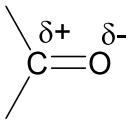

aldehyde ketone

bulkier alkyl groups in ketones hinder the approach of nucleophiles to the carbonyl carbon

### 4.1.1 Nucleophilic addition of HCN

| Students should be able to |
|---|
| *b) describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones* |
| *c) explain the differences in reactivity between carbonyls and alkenes towards nucleophilic reagent such as $LiAlH_4$ and HCN* |

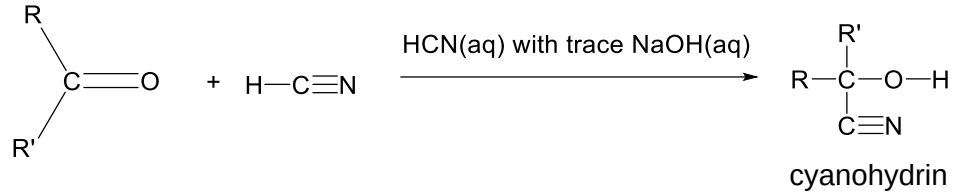
**Structure and reactivity**




- Although both alkenes and carbonyl compounds are **unsaturated** with double bonds, alkenes possess a C=C while carbonyl compounds possess a C=O. Hence, they **behave differently towards nucleophilic reagents**.
- Due to their unsaturation, **addition** reactions take place for both alkenes and carbonyl compounds. However, unlike the C=C bond which is non-polar, the C=O bond is **polar**. The **δ+ on the carbonyl C** atom makes it **susceptible to attack by nucleophiles**. On the other hand, the C=C of the alkene is electron-rich, disfavouring the approach of a nucleophile.

**Nucleophilic addition of carbonyl with HCN to from cyanohydrin**

Reagents and conditions: **HCN(aq) with trace NaOH(aq)**
*or* **HCN(aq) with trace NaCN(aq)/(s) as catalyst**




cyanohydrin

**Nucleophilic addition mechanism**

- The presence of a base, NaOH(aq) (*trace* amount) is required as
  - HCN is a weak acid which partially dissociates to give the nucleophile, $CN^-$

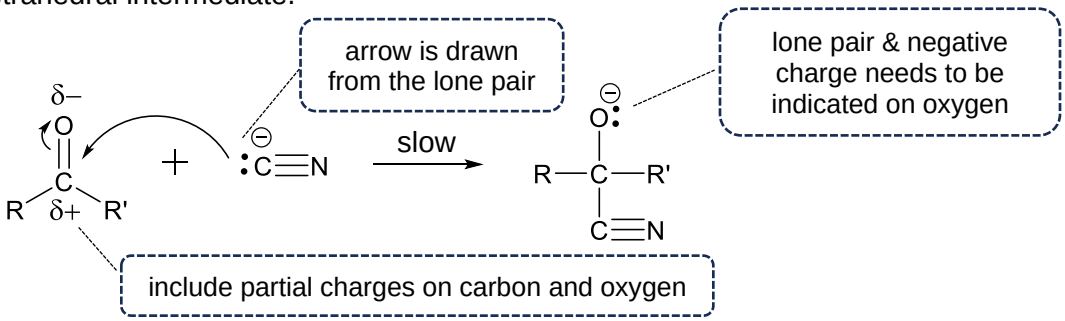
$$HCN \rightleftharpoons H^+ + CN^-$$

  - The base neutralises the HCN to give a water-soluble salt which dissociates to give the nucleophile, $CN^-$.

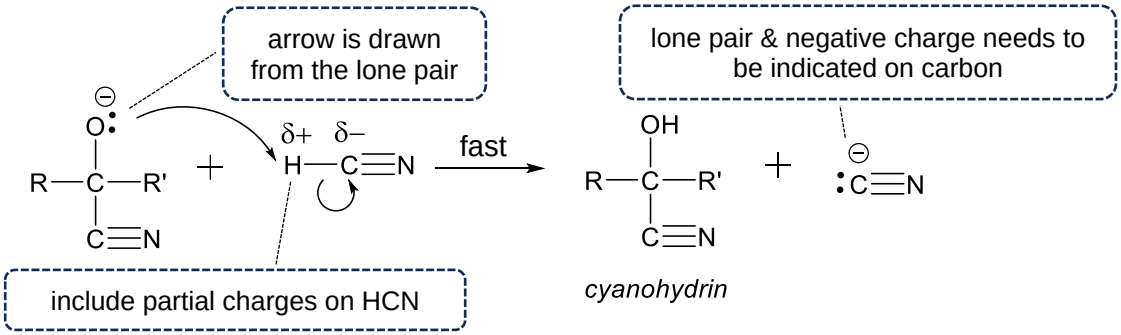
$$HCN + OH^- \rightarrow H_2O + CN^-$$

  - Alternatively, some NaCN(aq)/(s) is added to increase the amount of $CN^-$ present.
  - $CN^-$ is regarded as a catalyst as it is regenerated at the end of the reaction.

**Step 1**: Nucleophile $CN^-$ attacks the electron-deficient carbonyl carbon, giving the tetrahedral intermediate.



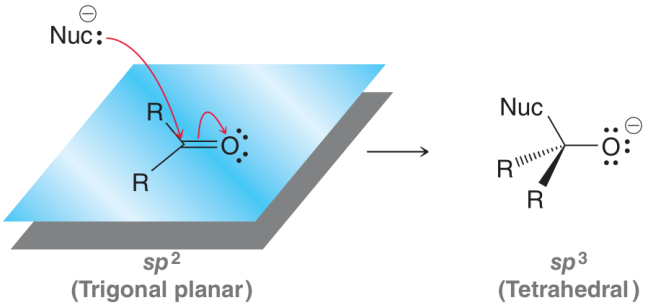

**Step 2**: The intermediate is protonated and the *catalyst* $CN^-$ is **regenerated**.




  - Rate = k[carbonyl][$CN^-$]
  - Any chiral product formed (e.g. $CH_3CH(OH)(CN)$) will be **optically inactive**.

- This is because the **carbonyl carbon** (e.g. in $CH_3CHO$) is **planar**. Nucleophiles can **attack from the top and bottom of the plane with equal probability**, giving rise to **a racemic mixture** of the product.

> **[Recall!]**
> *a racemic mixture contains equal amounts of the (+) and (–) enantiomers*




### 4.1.1.1 Reactions involving cyanohydrin

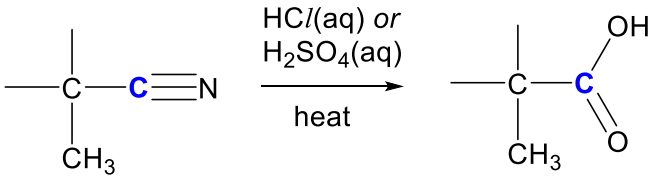
- Cyanohydrin is a useful intermediate in organic synthesis; it **increases** the number of carbon atoms in a reactant molecule (**step up reaction**). It can also be transformed into other functional groups.

> *cyanohydrin is a type of nitrile. Its reactions are similar to nitriles that you have learnt in halogen derivatives!*

#### (i) Hydrolysis

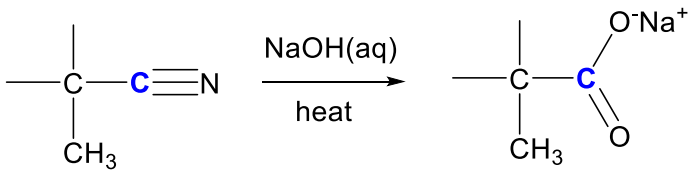
**<u>Acid hydrolysis of cyanohydrin to form carboxylic acid</u>**

Reagents and conditions: **heat with HC*l*(aq)**
*or* **heat with $H_2SO_4$(aq)**




**<u>Base hydrolysis of cyanohydrin to form carboxylate salt</u>**

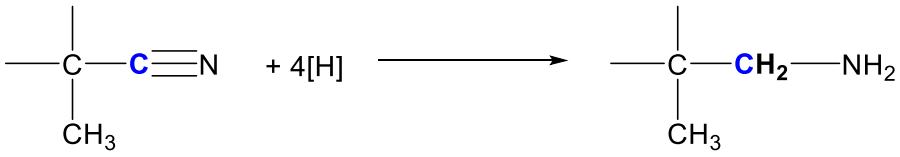
Reagents and conditions: **heat with NaOH(aq)**




#### (ii) Reduction

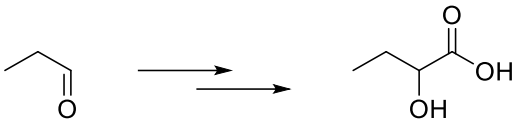
**<u>Reduction of cyanohydrin to form primary amine</u>**

Reagents and conditions: **Li*A*l$H_4$** (lithium aluminium hydride) **in dry ether**
*or* **$H_2$, Ni catalyst, heat**
*or* **$H_2$, Pt or Pd catalyst**



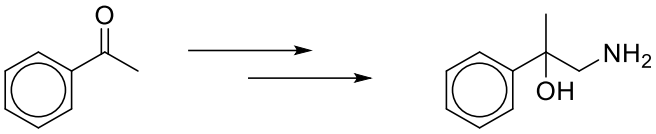
**Worked Example 3**

Provide reagents and conditions for the following multistep synthesis. Include structures of the intermediates.



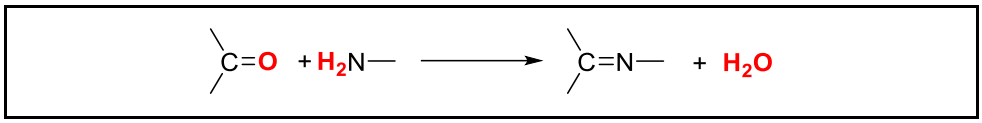

**Hint!**

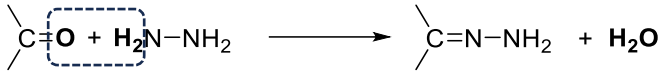
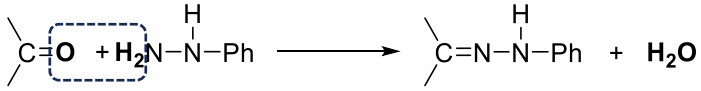
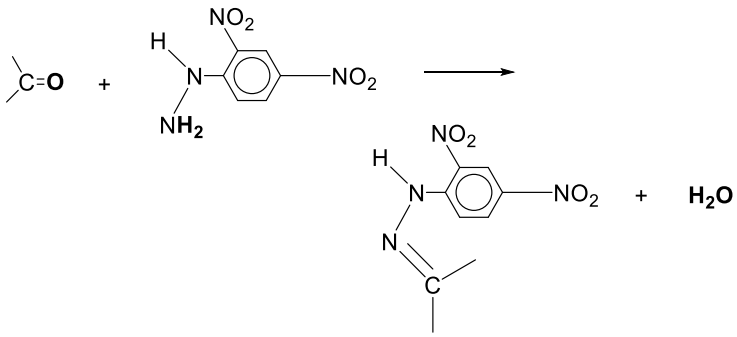
- there is an increase of **one carbon** in the product. What type of reaction could have caused this?
- note the functional group in the product and how it could have been derived




**You are now ready to attempt Tutorial Questions 1 to 3.**

### 4.1.2 Condensation reactions of >C=O with organic derivatives of ammonia



| condensation reagent | equation |
|---|---|
| hydrazine |  |
| phenylhydrazine |  |
| 2,4-dinitrophenyl-hydrazine<br><br>*also known as* 2,4-DNPH, Brady's reagent |  |

**Reaction with 2,4-dinitrophenylhydrazine – Test for carbonyl compounds**

| Students should be able to |
|---|
| *d) describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) to detect the presence of carbonyl compounds* |

2,4-dinitrophenylhydrazine (2,4-DNPH) is widely used to **identify the carbonyl *C=O*** functional group as the test is simple (simply add a few drops) and the product of condensation is obtained as an **orange precipitate**, with **sharp characteristic melting point**.

**Worked Example 4**

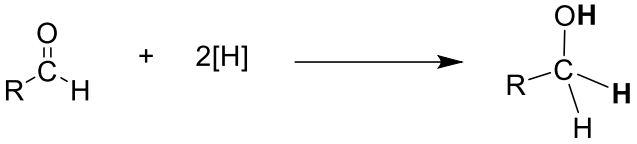
Write an equation to show the reaction between butanone and 2,4-DNPH.

## 4.2 Reduction of aldehydes and ketones

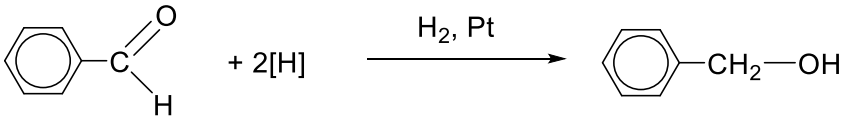
- Aldehydes ⟶ primary (1°) alcohols
- Ketones ⟶ secondary (2°) alcohols

Reagents and conditions: **$LiAlH_4$ in dry ether**
*or* **$NaBH_4$ in methanol or ethanol** (works in aqueous medium too!)
*or* **$H_2$, Ni catalyst, heat**
*or* **$H_2$, Pt catalyst**

**Reduction of aldehydes to primary (1°) alcohol**

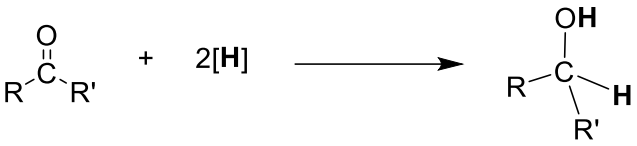



example:

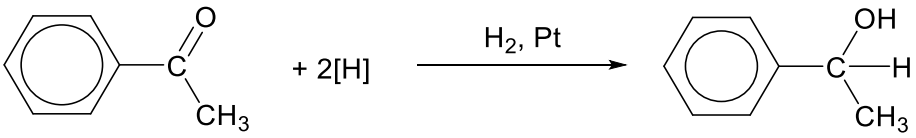



benzaldehyde (has an almond-like odour)

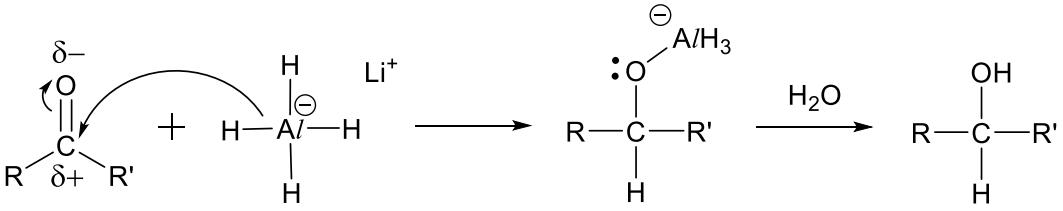
**Reduction of ketones to secondary (2°) alcohol**




example:




- The reduction of carbonyls with **nucleophilic reducing agents** ($LiAlH_4$ and $NaBH_4$) follow a nucleophilic addition mechanism.




$LiAlH_4$ and $NaBH_4$ cannot reduce alkenes as the nucleophilic reducing agents cannot attack an electron-rich C=C bond. Hence, $LiAlH_4$ and $NaBH_4$ are preferentially used for selective reduction of carbonyl in compounds that also contain C=C bond.

## 4.3 Oxidation of aldehydes (reducing property of aldehydes)

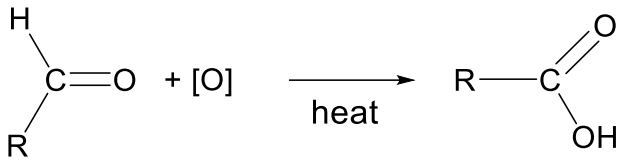
| Students should be able to |
|---|
| *e) deduce the nature (aldehyde or ketone) of an unknown carbonyl compound from the results of simple tests (i.e. Fehling's and Tollens' reagents; ease of oxidation)* |

- This *distinguishes* aldehydes from ketones as ketones CANNOT be oxidised under normal conditions.

### 4.3.1 With potassium dichromate or potassium manganate(VII)

**Oxidation of aldehyde to carboxylic acid**

Reagents and conditions: **$K_2Cr_2O_7$(aq), $H_2SO_4$(aq)**, **heat**
*or* **$KMnO_4$(aq), $H_2SO_4$(aq), heat**



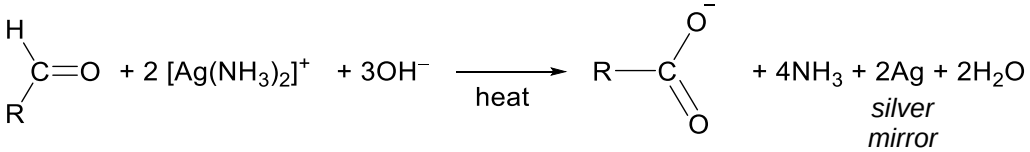

| reagent | observation |
|---|---|
| acidified $K_2Cr_2O_7$ | orange to green |
| acidified $KMnO_4$ | purple to colourless |

### 4.3.2 With Tollens' reagent (silver mirror test)

- Tollen's reagent is an alkaline solution of $[Ag(NH_3)_2]^+$, also known as diammine silver(I) complex or ammoniacal silver nitrate.
- Aldehydes reduce $[Ag(NH_3)_2]^+$ to *Ag* which is precipitated as a *solid silver (silver mirror).*

**Oxidation of aldehyde to carboxylate salt and silver mirror**

Reagents and conditions: **Tollens' reagent, heat**

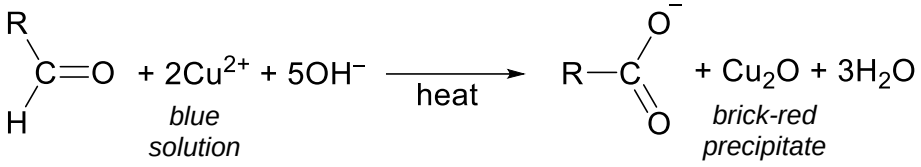



### 4.3.3 With Fehling's solution

- Fehling's solution is a blue alkaline solution of $CuSO_4$, potassium sodium tartrate and NaOH.
- *Aliphatic* aldehydes reduce $Cu^{2+}$ to copper(I) oxide, $Cu_2O$, a *brick-red precipitate*.
- Aromatic aldehydes do not react with Fehling's solution!

**Oxidation of aldehyde to carboxylate salt and Cu(I) oxide**

Reagent and conditions: **Fehling's solution, heat**

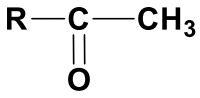



### 4.4 Tri-iodomethane formation (iodoform test)

Students should be able to

*f) deduce the presence of a $CH_3CO-$ group in a carbonyl compound from its reaction with alkaline aqueous iodine to form tri-iodomethane*

- Carbonyl compounds with the following structural unit (methyl carbonyl group)



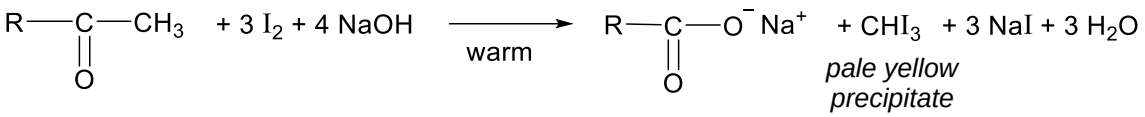

where R = H, alkyl or aryl

**[Recall!]**
*an alcohol with $CH_3CH(OH)-$ group also gives a positive iodoform test!*

give iodoform $CHI_3$, a **pale yellow precipitate** with an antiseptic smell.

**Iodoform Test** *(a type of oxidation or oxidative cleavage)*

Reagents and conditions: **$I_2$, NaOH(aq), heat**




- Negative test for $CH_3CO-$ in carboxylic acid $CH_3CO-OH$
  acyl chloride $CH_3CO-Cl$
  ester $CH_3CO-OR$
- Positive test for $RCOCH_3$ with iodide substituents like $RCOCH_2I$, $RCOCHI_2$, $RCOCI_3$

**Worked Example 5**

Which of the following carbonyls **do not** show a positive iodoform test?

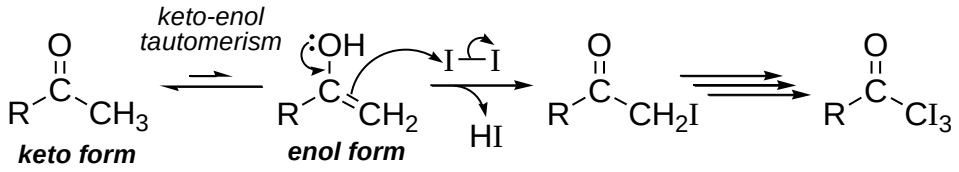
**A** $CH_3CHO$
**B** $CH_3CH_2CHO$
**C** $CH_3COCH_2CH_3$
**D** $C_6H_5COCH_3$

**You are now ready to attempt Tutorial Questions 4 to 7.**

**Additional information (not in syllabus)**

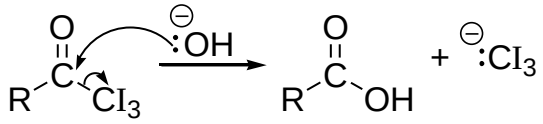
Mechanism of Tri-iodomethane Formation:

**Step 1**: electrophilic substitution of $-CH_3$ protons by I



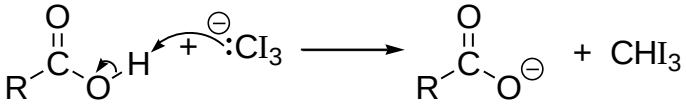

takes place via the **enol** form of the carbonyl compound.

**Step 2**: nucleophilic substitution of $-CI_3$ by –OH



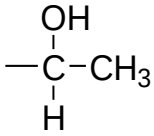
leading to the formation of **carbanion**, $^{\ominus}:CI_3$ , stabilised by presence of three electronegative I.

**Step 3**: proton transfer from $RCO_2H$ to $^{\ominus}:CI_3$



giving products, carboxylate ion and iodoform, $CHI_3$.

Note:



which give positive iodoform test are first oxidised by $IO^-$ from the $I_2$/NaOH mixture

$\left(I_2 + 2OH^- \rightarrow I^- + IO^- + H_2O\right)$ to the corresponding methyl ketone: