ANDERSON SERANGOON JUNIOR COLLEGE

JC2 H2 CHEMISTRY

CARBONYL COMPOUNDS

Guiding Questions

1. How are carbonyl compounds synthesised?
2. Which class of reagents do carbonyl compounds react with and why? What types of reactions do carbonyl compounds undergo and why?
3. How do carbonyl compounds react with HCN in nucleophilic addition?

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

References

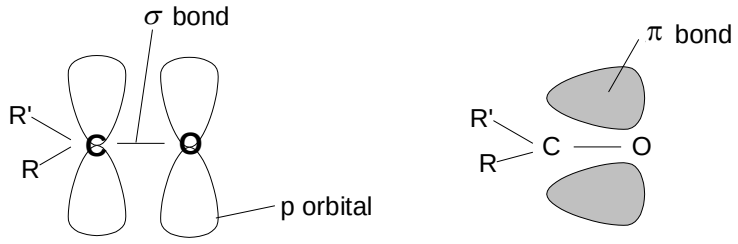
1. Chemistry for Advanced Level, Cann and Hughes, Murray
2. A–Level Chemistry by E.N. Ramsden
3. Understanding Chemistry for Advanced Level by Ted Lister and Janet Renshaw
4. Chemistry in Context by Graham Hill and John Holman

Part I: Introduction

(A) The carbonyl group

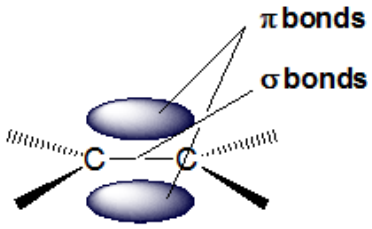
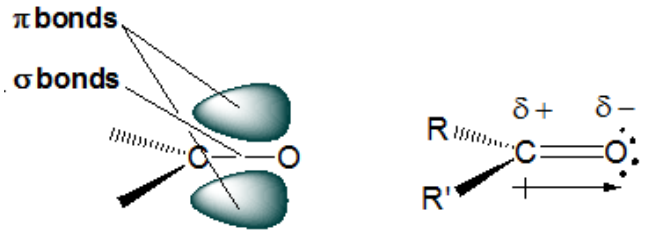
- The carbonyl group, $>C{=}O$, is present in aldehydes and ketones.

Bonding in the carbonyl group: σ and π bond in carbonyl group



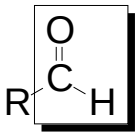
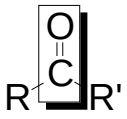
- The carbonyl carbon is sp^2 hybridised and forms three σ bonds, which are planar.
- The unhybridised p orbital of the carbon atom overlaps sideway with the adjacent p orbital of the oxygen atom to form a π bond.

Comparison between alkene and carbonyl group

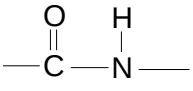
Alkene	Carbonyl
 even electron density in alkene	 electron density pulled closer to electronegative carbonyl oxygen
• **Electron cloud is evenly distributed** between the two sp^2 hybridised carbon atoms. • **Electron–rich C=C attracts electrophiles** (electron–loving species) like $\overset{\delta+}{H}-\overset{\delta-}{Br}$.	• Electrons in the σ and π bonds are drawn towards the **more electronegative oxygen atom**. This makes the carbonyl group **polar**: $C_{\delta+} = O_{\delta-}$, creating an **electron–deficient carbon atom**. • The electron–deficient carbon **attracts nucleophiles** like CN^- and H^- (from $LiAlH_4$).

(B) Aldehydes and Ketones

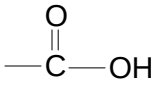
1. General formula for both homologous series is **$C_nH_{2n}O$**.
2. The carbonyl groups in aldehydes and ketones differ in their positions in the carbon chain.

Aldehydes	Ketones
	
• Carbonyl group is at the **end of carbon chain** • **RCHO** represents the **aldehyde functional group**. (Do not write as "RCOH", as it may indicate that the molecule possesses an –OH group)	• Carbonyl group is **between the carbon chain** • **RCOR'** represents the **ketone functional group**, where R and R' are alkyl or aryl groups and not H atom.

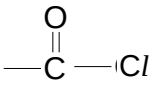
Note that the following compounds, though contain carbonyl group, have different reactive groups (functional groups) as that of aldehyde or ketone.



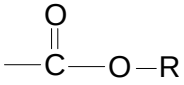
Amide



Carboxylic Acid



Acyl Chloride



Ester

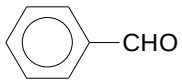
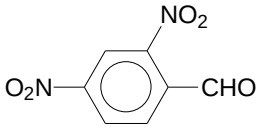
Part II: Nomenclature of carbonyl compounds

(A) Naming Aldehydes

1. Identify the longest continuous chain that contains the –CHO group and the –CHO carbon is numbered as C–1. The alkane name provides the parent name.
2. Replace ***–e*** of the alkane name by ***–al***.
3. Substituents are named as usual.

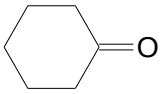
Structural formula	Name
HCHO	methanal
CH_3CHO	ethanal
$CH_3CH(CH_3)CHO$	
$CH_3CH{=}CHCHO$	

4. For aromatic aldehydes (in which –CHO is directly bonded to benzene), the parent name is **benzaldehyde**. Substituents are named as usual.

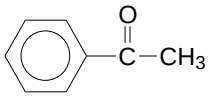
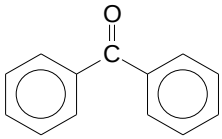
Structural formula	Name
	benzaldehyde
	

(B) Naming Ketones

1. Identify the longest continuous chain that contains the >C=O group. The alkane name provides the parent name.
2. Replace the ***–e*** of the alkane name by ***–one***.
3. Ensure **lower numbering** is used to locate the >C=O group (for 5 carbons and above).
4. Substituents are named as usual.

Structural formula	Name
CH_3COCH_3	propanone
$CH_3CH_2COCH_3$	butanone
$CH_3CH_2CH_2COCH_2CH_3$	hexan–3–one
$CH_3CH_2\underset{\displaystyle CH_3}{\underline{C}}HCO\underset{\displaystyle CH_3}{\underline{C}}HCH_3$	
	cyclohexanone

5. For aromatic ketones (in which >C=O is **directly** bonded to benzene ring), the benzene ring is named as substituent – **phenyl**.

Structural formula	Name
	phenylethanone
	diphenylmethanone

Part III: Physical Properties of carbonyl compounds

(A) Boiling points

1. Aldehydes and ketones have **higher** boiling points than alkanes of similar molecular mass but **lower** boiling points than alcohols.

   Explanation: >C=O group is polar.
   Permanent dipole–permanent dipole (pd–pd) attractions between polar aldehyde and ketone molecules are **stronger** than the instantaneous dipole–induced dipole (id–id) attractions between non–polar alkane molecules but **weaker** than the hydrogen bonds between polar alcohol molecules.

Type of compound	Compound	Structure	Molecular mass	Boiling point (°C)
alkane	ethane	$CH_3—CH_3$	30	−89
aldehyde	methanal	$H—CHO$	30	−21
alcohol	methanol	$CH_3—OH$	32	65
alkane	propane	$CH_3—CH_2—CH_3$	44	−42
aldehyde	ethanal	$CH_3—CHO$	44	20
alcohol	ethanol	$CH_3—CH_2—OH$	46	78
alkane	butane	$CH_3—CH_2—CH_2—CH_3$	58	−1
aldehyde	propanal	$CH_3—CH_2—CHO$	58	49
alcohol	1-propanol	$CH_3—CH_2—CH_2—OH$	60	97

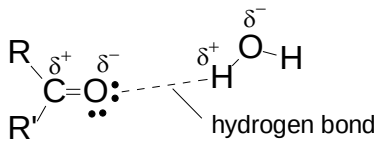
Table 1: Comparison of boiling point of alkane, aldehyde and alcohol

(B) Solubility in polar solvents

1. Shorter chain aldehydes and ketones are **soluble in polar solvents**.

   Explanation for higher water solubility compared to alkanes:
   The carbonyl oxygen can form hydrogen bonds with water molecules.
   The energy released during the formation of hydrogen bonding between carbonyl compound molecules and water molecules is able to compensate for the energy taken in to break the permanent dipole - permanent dipole attractions between carbonyl compound molecules and the hydrogen bonding between water molecules.

Hydrogen bonds between carbonyl compound and water molecules



Class	Example	Formula	Molecular weight	Boiling point (°C)	Water solubility
Alkane	butane	$CH_3CH_2CH_2CH_3$	58	0	Insoluble
Aldehyde	propanal	$CH_3CH_2—\overset{\overset{O}{\|\|}}{C}—H$	58	49	Soluble
Ketone	propanone (acetone)	$CH_3—\overset{\overset{O}{\|\|}}{C}—CH_3$	58	56	Soluble
Alcohol	1-propanol	$CH_3CH_2CH_2—OH$	60	97	Soluble

Table 2: Physical properties of aldehyde and ketone

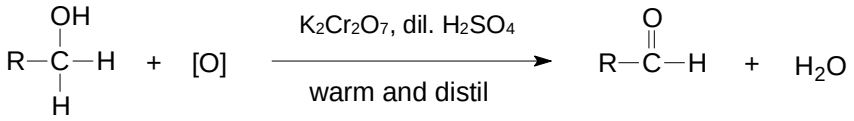
2. As the non–polar alkyl chain gets longer, the **solubility in water decreases**.

   Explanation: As the size of the non–polar alkyl chain increases, the instantaneous dipole–induced dipole (id–id) attractions become more significant. Hence, the energy evolved during the formation of hydrogen bonding between the water molecules and the carbonyl compound molecules is not enough to compensate for the energy required to break the stronger id-id attractions between carbonyl compound molecules and the hydrogen bonding between water molecules.

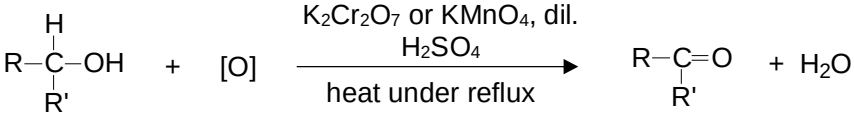
Part IV: Preparation of aldehydes and ketones

(A) Aldehydes and ketones are obtained by **oxidation** of the corresponding alcohols.

Primary alcohols undergo oxidation to aldehydes

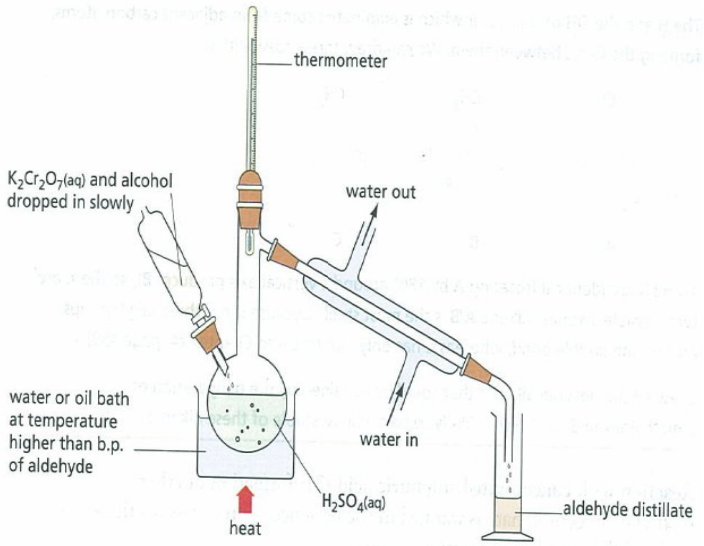


Secondary alcohols undergo oxidation to ketones



"Recall from Hydroxy Compounds"

- The aldehyde is **distilled** off as soon as it forms, to avoid further oxidation.
- Acidified potassium manganate(VII) is **not** used as oxidising agent as the primary alcohol will be oxidised to carboxylic acid.



Chemistry for Advanced Level, Peter Cann, 2002

Exercise 1:

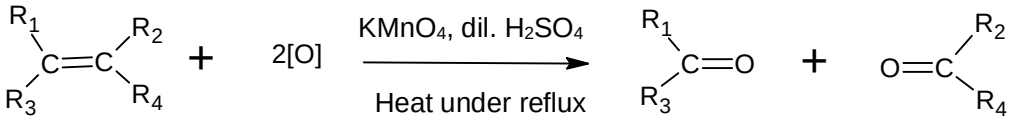
Oxidation is an important reaction in organic chemistry. Both aldehydes and carboxylic acids can be prepared by the oxidation of primary alcohols with acidified $K_2Cr_2O_7$.

Describe how you could ensure that only either the aldehyde or the carboxylic acid is produced during the oxidation process.

Answer:

*To produce only the aldehyde: _____ the _____ **alcohol** with $K_2Cr_2O_7$, H_2SO_4 and _____.*
*To produce only the carboxylic acid: _____ the _____ **alcohol** _____ with $K_2Cr_2O_7$, H_2SO_4.*

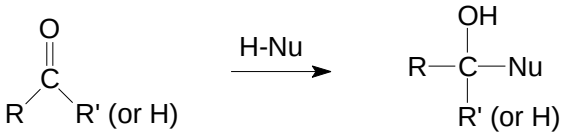
NOTE: Recall strong oxidising agents, e.g. hot $KMnO_4$ (not $K_2Cr_2O_7$) can cleave some specific C=C bonds to produce ketones (Refer to 'Alkenes' lecture notes.)



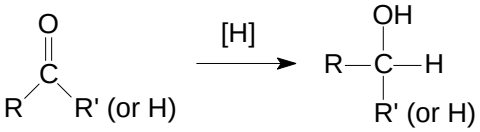
However, this reaction is not commonly used to prepare ketones.

Part V: Reactions of Carbonyl Compounds

(A) Nucleophilic addition

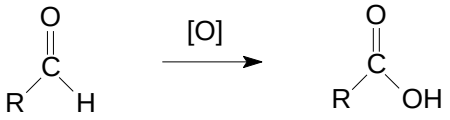


(B) Reduction



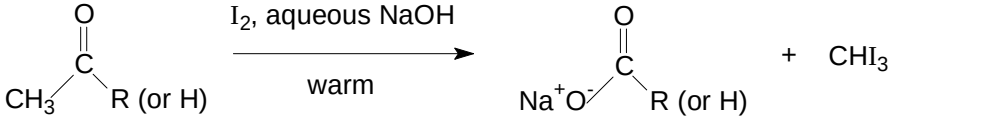
alcohol

(C)(I) Oxidation



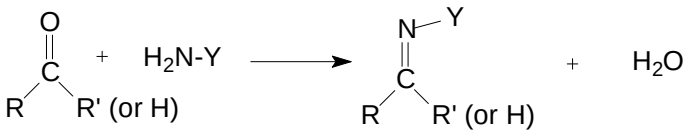
aldehyde only carboxylic acid

(C)(II) Tri–iodomethane (iodoform) reaction (oxidation)



sodium salt tri-iodomethane

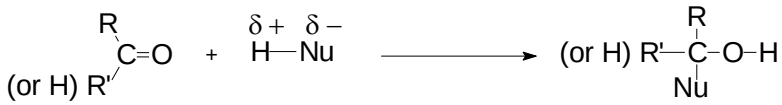
(D) Condensation (addition–elimination)



hydrazone

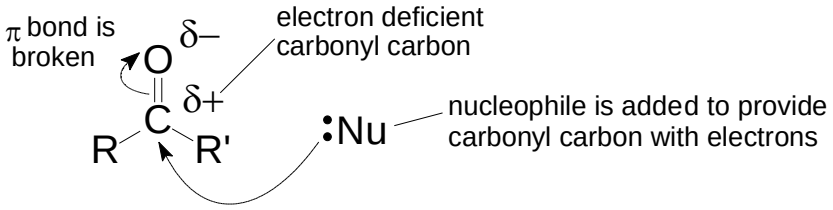
(A) Nucleophilic Addition

The most common reaction of aldehydes and ketones is the **nucleophilic addition reaction**.



Why do aldehydes and ketones undergo nucleophilic addition reaction?

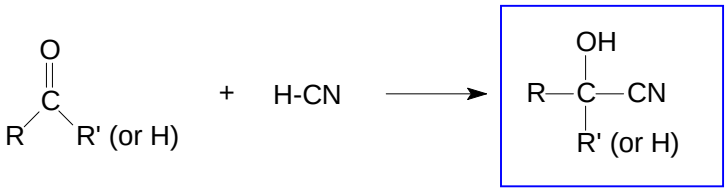
- >C=O is polar with carbonyl carbon having **partial positive charge**. The carbonyl carbon is **electron–deficient** and thus is susceptible to attack by a **nucleophile**.
- The attack on the electrophilic carbon breaks the **carbonyl π bond** and the nucleophile is **added** to the carbonyl C.



Why do aldehydes and ketones NOT undergo nucleophilic substitution reaction?

The carbonyl functional group is either bonded to two other carbon atoms (as in ketone) or a carbon atom and a hydrogen atom (as in aldehyde). If the carbonyl compound is to undergo nucleophilic substitution, then **either the C–C bond or the C–H has to be broken**. The **breaking of these two types of bonds is energetically demanding and the carboanion (R^-) / hydride (H^-) formed is a poor leaving group (they are strong bases).**

Nucleophilic addition with hydrogen cyanide (HCN)



cyanohydrin

Reagent: **HCN**
Condition: **Cold,** and with presence of **NaCN or KCN** as **catalyst**
OR with presence of **trace amount of base** such as **NaOH**

OR
Reagent: **KCN / NaCN**
Condition: **dilute H_2SO_4** (to give a slightly acidic conditions)

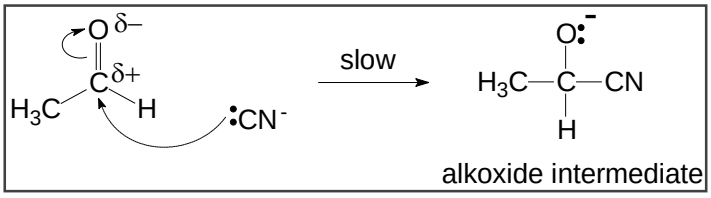
Note: In a highly acidic condition, CN^- will be protonated to become HCN. This will decrease the $[CN^-]$ and reduce the rate of nucleophilic addition.

[*Advantage of the latter*: high $[CN^-]$ which speeds up the nucleophilic addition reaction (see p12)]

Mechanism for Nucleophilic Addition [when HCN is used]

Step 1: Nucleophilic attack by CN^- (slow step)

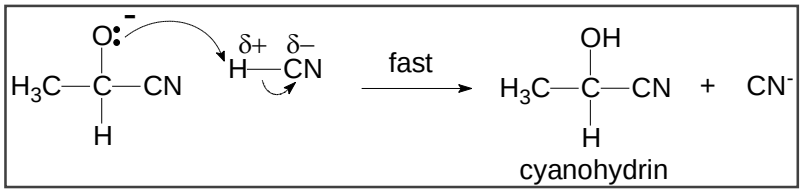
The nucleophile*, CN^-, is attracted by the electron–deficient carbon atom. As CN^- approaches, the π electrons are repelled away from the carbon atom towards the oxygen atom.



** CN^- is generated either from the catalyst used or from the increased extent of ionisation of HCN due to trace amount of NaOH added.*

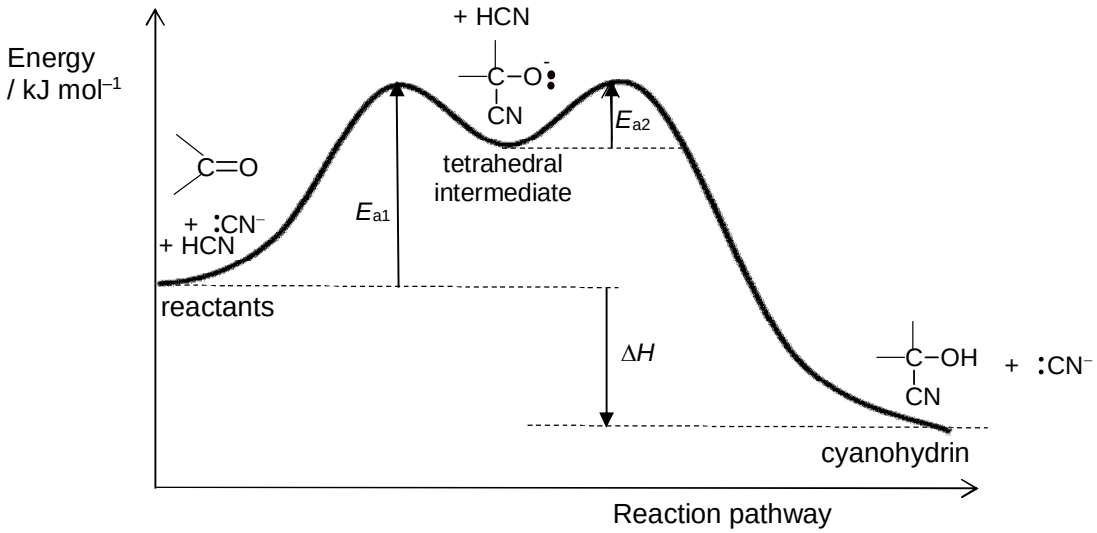
Step 2: Protonation of the intermediate (fast step)

The intermediate alkoxide anion is a strong base. It can abstract a proton (H^+) from an un–ionised molecule of HCN. The homogeneous catalyst, CN^-, is regenerated.



√*Checklist:*
- *show full headed arrow from electron pair donor to electron pair acceptor*
- *label slow and fast step*
- *indicate dipoles on >C=O, lone pair on nucleophile*
- *draw the correct alkoxide intermediate & CN^- ion must be regenerated at the end of the reaction*

Energy profile diagram

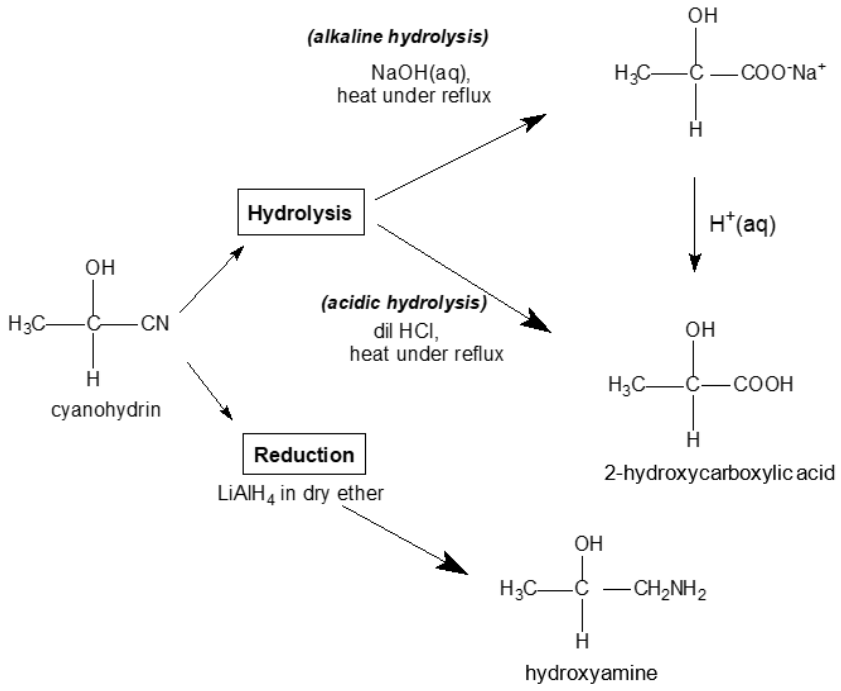


Importance of HCN addition reaction with carbonyl compounds

1. It is a method for **lengthening of carbon chain** (CN^- increases the chain by one carbon atom.)
2. _____ of cyanohydrin produces an important group of compounds called **2–hydroxycarboxylic acids**.
3. _____ of cyanohydrin produces another important group of compounds called **hydroxyamines.**

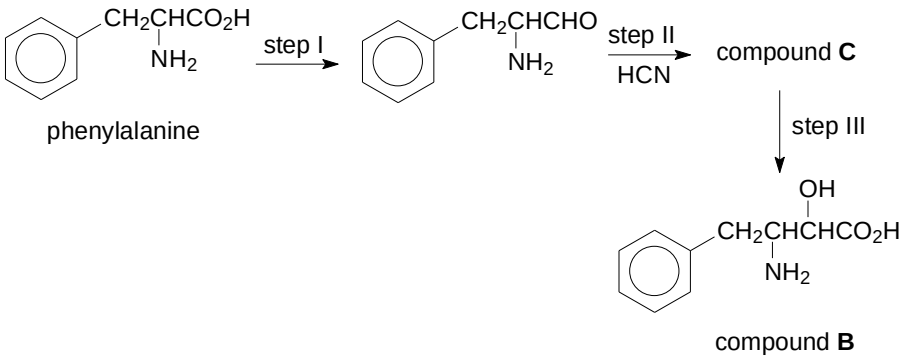
Reactions of cyanohydrin to produce 2–hydroxycarboxylic acids and hydroxyamines

- The **nitrile, –CN**, functional group in the cyanohydrin molecule can undergo two types of reactions
  - **hydrolysis to a carboxylic acid** (or salt; in alkaline condition) and,
  - **reduction to an amine**, as shown below.



Exercise 2:

B can be synthesised from the naturally occurring amino acid phenylalanine by the following route.



(a) Draw the structure of the intermediate compound **C**.

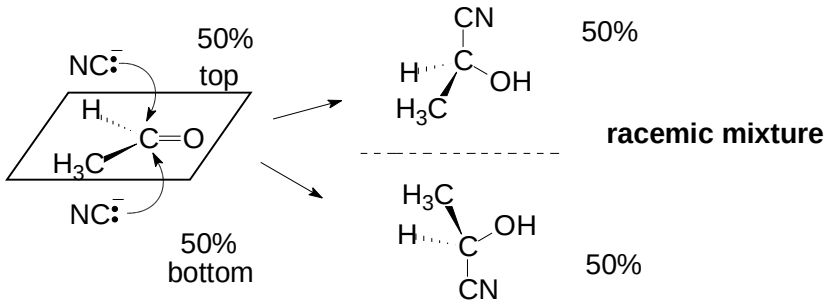
(b) Step III is a hydrolysis reaction. Draw the structural formula of the organic product formed when **C** is hydrolysed by *(Hint: the carboxylic acid group is acidic whilst an amine is basic)*

(i) an excess of hydrochloric acid

(ii) an excess of aqueous sodium hydroxide.

Stereochemistry of Nucleophilic Addition Reaction

The carbonyl molecule is trigonal planar with respect to the carbonyl carbon. The nucleophile is equally likely to attack from either side of the plane. Hence, for all aldehydes and asymmetrical ketones, an optically inactive **racemic mixture, containing equimolar amounts of the two enantiomers, will be formed**.



Factors affecting Rate of Nucleophilic Addition Reaction

1. **Catalyst is important** because the reaction is slow in the absence of a catalyst.

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

HCN is a weak acid which ionises partially. [CN^-] is low. This results in a slow rate of nucleophilic addition. Addition of a catalyst (NaCN or KCN) **increases the concentration** of the CN^-.

The use of a trace amount of base e.g. NaOH also **increases the concentration** of the CN^- since the presence of OH^- shifts the position of the above equilibrium to the right.

From the rate–determining step, rate = *k* [carbonyl] [CN^-]. Thus, an increase in concentration of CN^- will increase the rate of reaction.

2. **pH of the reaction medium** affects reaction rate.

Condition	Relative rate of nucleophilic addition	Reasons for differences in rate
Acidified solution		[H^+] is high. Ionisation of HCN is suppressed and [CN^-] is **low** hence rate is **slow**.
Slightly alkaline solution		[CN^-] is **high** hence rate is **rapid**.
Very alkaline solution		OH^- nucleophile will compete for the carbonyl carbon in the addition reaction.*

** (FYI) Beside the competing nucleophile effect, a side–reaction (Aldol addition) could take place and thus further reduces the rate.*

3. Ketones tend to be _____ than aldehydes in nucleophilic addition due to the presence of an additional alkyl group bonded to the carbonyl carbon atom of the ketone.

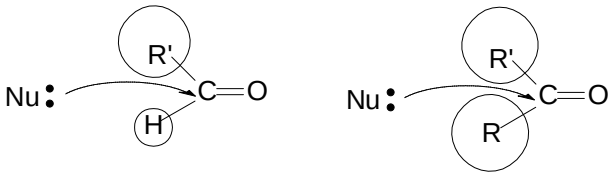
Reasons:

Electronic effects

a. The additional alkyl group has electron–donating effect which reduces the partial positive charge on the carbonyl carbon, making it less susceptible to attack by nucleophiles.

Steric hindrance

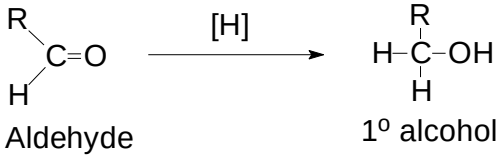
b. The additional alkyl group is bulky and results in greater steric hindrance which hinders the approach of nucleophiles to the carbonyl carbon.



steric hindrance in ketones

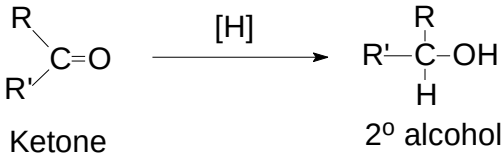
(B) Reduction of carbonyl compounds

Aldehyde reduces to primary alcohol



Aldehyde → 1º alcohol

Ketone reduces to secondary alcohol



Ketone → 2º alcohol

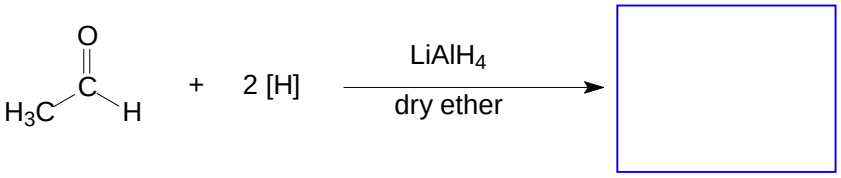
Reagents and Conditions

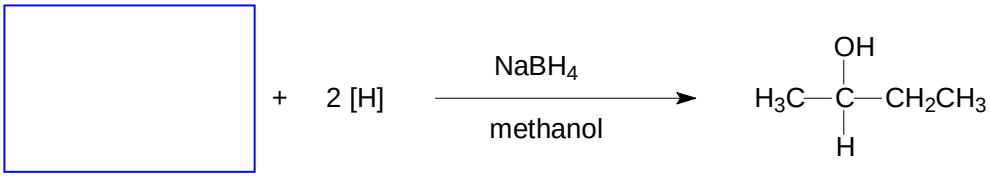
i. **$LiAlH_4$ in dry ether, r.t.**
ii. **$NaBH_4$ in methanol, r.t.**
iii. **H_2 over Pt / Pd, r.t.p. or H_2, Ni, heat**

Note:

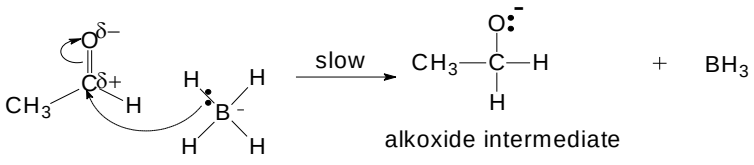
- **Like alkenes, carbonyl compounds** can be **reduced by H_2 gas over Ni, Pt, or Pd** catalyst via heterogeneous catalysis mechanism.
- **$LiAlH_4$ and $NaBH_4$** attack polar bonds. They **do not** reduce both >C=C< and –C≡C– bonds.
- **$LiAlH_4$** reduces a wider range of organic compounds, e.g. carboxylic acids, esters, amides, nitriles, aldehydes and ketones. However, **$NaBH_4$ only** reduces aldehydes and ketones.

Exercise 3:

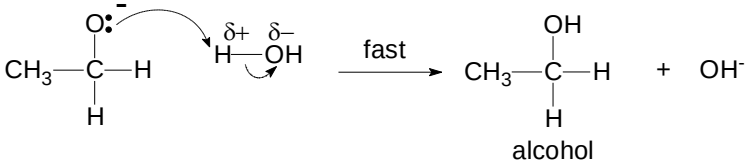




Mechanism of complex metal hydride reduction:
A nucleophilic addition reaction takes place and an alkoxide intermediate is formed. The resulting alkoxide ion is protonated by water to give an alcohol.



alkoxide intermediate



alcohol

(C)(I) Oxidation of carbonyl compounds

- **Oxidation of aldehydes by strong oxidising agents**
  Aldehydes are easily oxidised to carboxylic acids.

Aldehyde — Carboxylic acid

Heating with	Observations
$KMnO_4$, dil. H_2SO_4	purple colour of MnO_4^- decolourised
$KMnO_4$, dil. NaOH	purple colour of MnO_4^- decolourised and brown ppt of MnO_2 formed
$K_2Cr_2O_7$, dil. H_2SO_4	orange colour of $Cr_2O_7^{2-}$ turned green

- **Oxidation of ketones by strong oxidising agents**
  Ketones are not readily oxidised as they do not have a hydrogen atom attached directly to the carbonyl carbon.

Ketone

- **Oxidation of aldehydes by mild oxidising agents**
  Two common mild oxidising agents used are **Tollens' reagent** and **Fehling's solution**.
  Under the alkaline conditions in these reagents, the aldehyde is oxidised to **the salt of the corresponding carboxylic acid.**

Tollens' reagent (positive test for both aliphatic and aromatic aldehydes)

– a complex of diamminesilver(I) ions, $\mathbf{[Ag(NH_3)_2]^+}$, in alkaline solution

Condition: warm

$$2[Ag(NH_3)_2]^+ + RCHO + 3OH^- \rightarrow \underset{\text{carboxylate ion}}{RCOO^-} + \underset{\text{silver mirror}}{2Ag} + 4NH_3 + 2H_2O$$

Observation:
For **aliphatic** aldehyde, _____ is formed on the walls of the test-tube.

For **aromatic** aldehyde, **silver mirror is also formed (on standing).**

Fehling's solution (positive test only for aliphatic aldehydes)

– a complex of **Cu^{2+} in alkaline solution**

Condition: warm

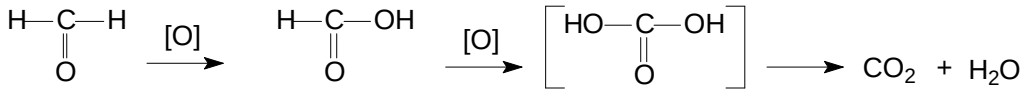
$$2Cu^{2+} + RCHO + 5\,OH^- \rightarrow \underset{\text{carboxylate ion}}{RCOO^-} + \underset{\text{red–brown ppt}}{Cu_2O} + 3H_2O$$

Observation:
For **aliphatic aldehyde**, **a red-brown (brick–red) ppt, Cu_2O,** will be formed and blue Fehling's reagent is decolourised.

Cu(II) ions in Fehling's solution cannot oxidise aromatic aldehydes e.g. benzaldehyde.
Thus, for **aromatic aldehyde**, **no red–brown (brick–red) ppt** and Fehling's reagent remains blue.

Note:

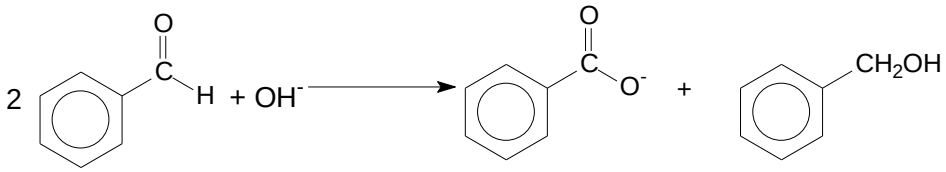
Methanal (HCHO) is a more powerful reducing agent than other aldehydes.
While other aldehydes reduce Cu(II) only to Cu(I), methanal can reduce Cu(II) to Cu(0) (itself oxidised to CO_2 and H_2O).



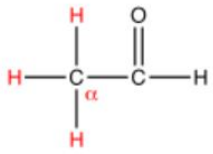
methanal — methanoic acid — carbonic acid

Observation: Mixture of red–brown ppt of Cu_2O and shiny pink metal of Cu

FYI: Under the influence of NaOH(aq) from Fehling's solution, one molecule of benzaldehyde oxidises another benzaldehyde molecule and is itself reduced to the alcohol:

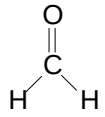
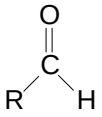
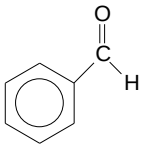
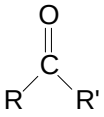


The mechanism of this **disproportionation** reaction is similar to the reduction of carbonyl compounds using complex metal hydrides.
This reaction is known as the **Cannizzaro reaction**. It can also occur with any aromatic aldehydes and aldehyde that lacks an α H atom on the *C atom next* to the >C=O group (the α carbon).



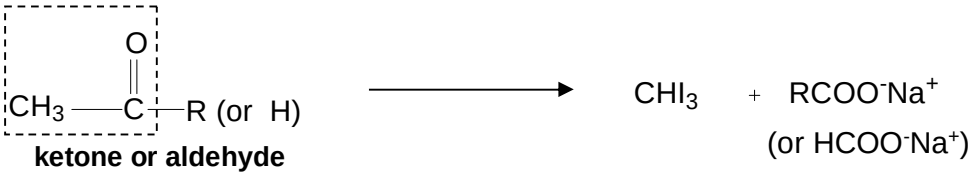
Summary of mild oxidation reactions of aldehydes

Aldehydes and ketones can be readily distinguished from the way they react with oxidising agents.

	most readily oxidised ⟶ **least readily oxidised**			
Carbonyl compound	methanal	aldehydes (except methanal)	benzaldehyde	ketones
				
Warm with Tollens' reagent	silver mirror	silver mirror	silver mirror (upon standing)	no silver mirror observed
Warm with Fehling's solution	mixture of brown ppt (Cu_2O) and shiny pink metal (Cu)	red–brown ppt (Cu_2O)	no red–brown ppt observed	no red–brown ppt observed

(II) Oxidation with I_2(aq) in NaOH(aq) (Iodoform reaction)

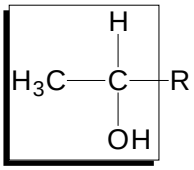
Aldehydes and ketones with the general formula **CH_3COR** where R is a H atom or an alkyl group can undergo iodoform reaction to produce **tri–iodomethane CHI_3** and **a carboxylate salt.**



Reagent and condition: **I_2(aq) in NaOH(aq), warm**

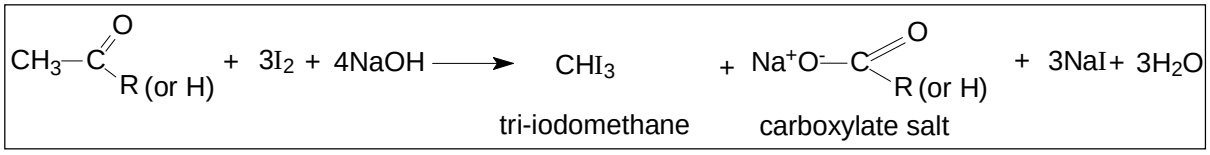
Observation: _____ **(CHI_3)**

Recall:



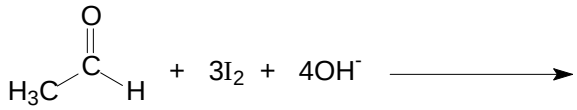
Tri-iodomethane test for alcohol

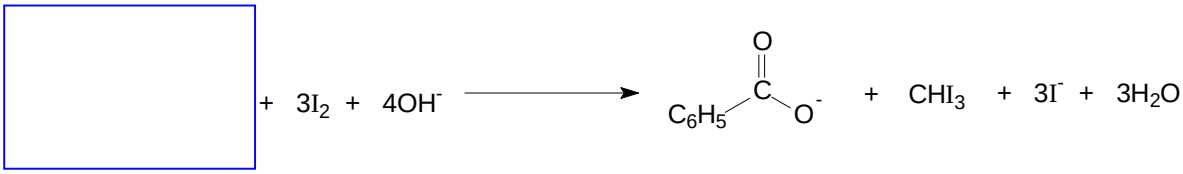
General Equation:

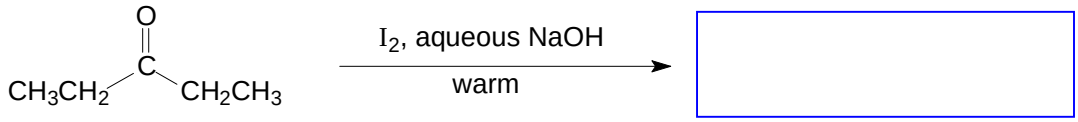


Note that the carboxylate ion formed has 1 less C atom than the starting carbonyl compound. Thus, it is a step–down reaction.

Exercise 4:

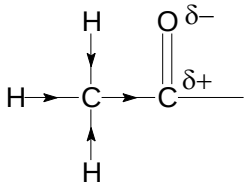




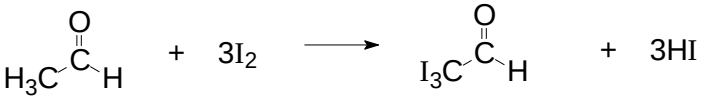


Explanation for tri–iodomethane reaction:

1. The polar carbonyl group with partially positive carbonyl carbon has **electron–withdrawing effect** on neighbouring carbon atoms.

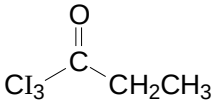


2. C–H bonds of neighbouring carbon atom are more polar and thus the H atoms are **more readily substituted** by iodine.



3. Subsequent hydrolysis with aqueous NaOH produces the yellow ppt CHI_3 and the sodium salt.

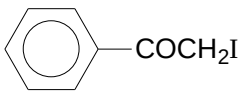
***Question**:* Can this compound give positive tri-iodomethane test?



Exercise 5: N2010/I/25

Which compound will **not** give tri–iodomethane on warming with alkaline aqueous iodine?

A $CH_3COCHClCOCH_3$

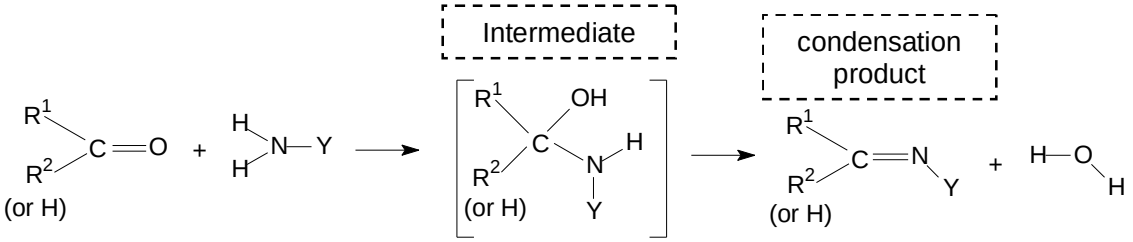
B 

C $I_2CHCH(OH)CO_2H$

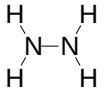
D $CI_3CO_2CH_3$

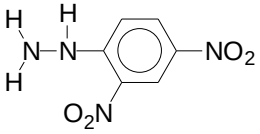
(D) Condensation (or addition–elimination) Reaction

- When carbonyl compounds react with ammonia derivatives, condensation reaction occurs where an **addition** reaction is followed by **elimination** of a simple molecule such as H_2O or NH_3.



Some examples of ammonia derivatives:


hydrazine

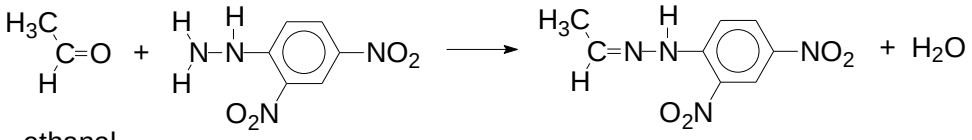

2,4-dinitrophenylhydrazine (2,4-DNPH)

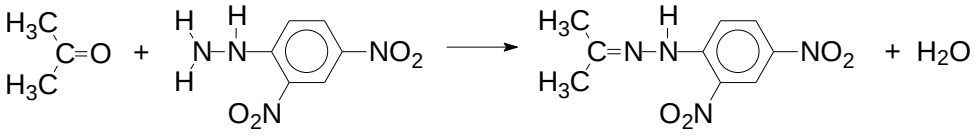
Condensation with 2,4–dinitrophenylhydrazine (2,4–DNPH)

Aldehydes and ketones undergo condensation reaction with **2,4–dinitrophenylhydrazine (2,4–DNPH)** to form products known as hydrazone, which are **crystalline solids** with **well–defined melting points**.

a) Yellow or orange crystalline solids indicate the presence of **aldehydes and ketones**.
b) Well–defined melting points of hydrazones help to **identify** the aldehydes and ketones.

Example:


ethanal — orange hydrazone

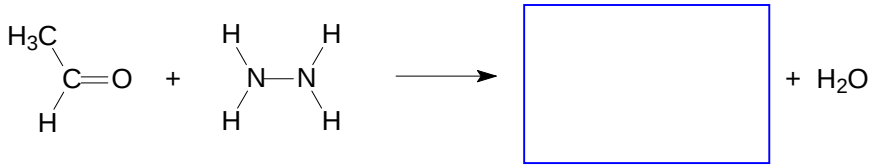

propanone — orange hydrazone (m.p: 126 ^oC)

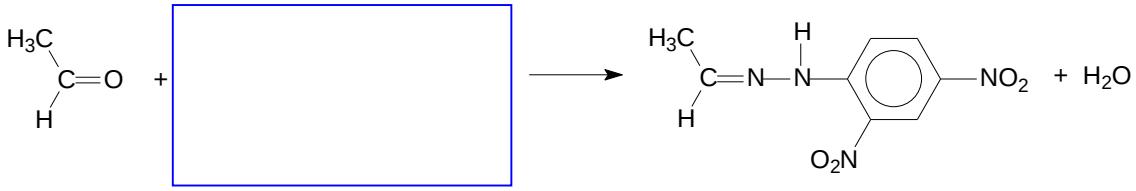
Reagent: **2,4–dinitrophenylhydrazine (2,4–DNPH)**

Condition: **warm**

Exercise 6:

Draw the structure of the missing compound in the following questions.

(a) 

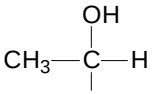
(b) 

Exercise 7:

State possible reagent(s) to distinguish the following compounds.

(a)	CH_3COCH_3 and $CH_3CH_2CH_2OH$	
(b)	$C_2H_5COC_2H_5$ and $CH_3CH_2CH_2CH_2CHO$	
(c)	CH_3COCH_3 and $C_2H_5COC_2H_5$	
(d)	C_6H_5CHO and CH_3CHO	

Part VI: Chemical Tests for Carbonyl Compounds

	Test			
	2,4–dinitrophenylhydrazine (2,4–DNPH) or Brady's reagent	**Tollens' reagent (or silver mirror)**	**Fehling's solution**	**Tri–iodomethane (iodoform) reaction**
Procedure	Add 2,4–DNPH to unknown substance and warm the mixture	Add Tollens' reagent to unknown substance, warm and allow to stand	Add Fehling's solution to unknown substance and warm	Add aqueous iodine in aqueous NaOH to unknown substance and warm
Observation for positive test	yellow or orange (crystalline) ppt	shiny silvery deposit (solid) or silver mirror on walls of test–tube or black or grey deposit	red–brown ppt (Cu_2O)	yellow ppt (CHI_3)
Purpose	distinguish carbonyl compounds (aldehydes and ketones) from other functional groups (FGs)	distinguish aldehydes from ketones and other FGs	distinguish aliphatic aldehydes from ketones and other FGs	distinguish carbonyl compounds with $CH_3CO–$ group or alcohols with  group in their structure from other aldehydes/ketones or other FGs
Functional group				
aliphatic aldehyde	+	+	+	+ (only ethanal)
benzaldehyde (or aromatic aldehydes)	+	+	–	–
ketone	+	–	–	+ (for compounds with $CH_3CO–$ group)
other functional groups	–	–	–	– (except alcohols with $CH_3CH(OH)–$ group)