Raffles Institution
Year 6 H2 Chemistry 2023
Lecture Notes 17 – Carbonyl Compounds

Lecturer: Dr Jackson Koh

I Learning Objectives

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

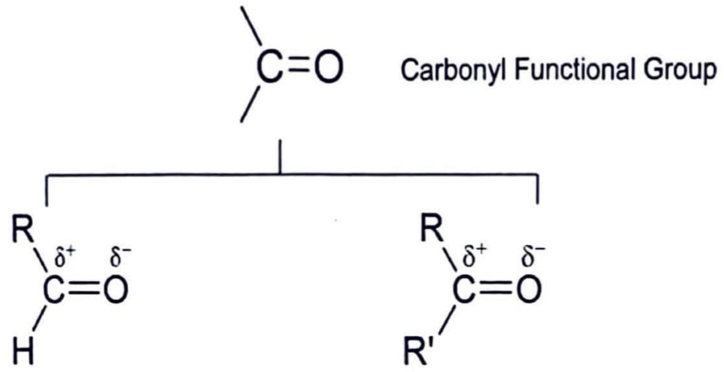
II References

1. Understanding Advanced Organic and Analytical Chemistry by Kim Seng Chan & Jeanne Tan.
2. Chemistry in Context by G. C. Hill & J. S. Holman
3. 'A' Level Chemistry by E. N. Ramsden
4. Organic Chemistry by John McMurry

III Contents

1 INTRODUCTION

1.1 Carbonyl Compounds – Aldehydes & Ketones



Aldehyde

Ketone

- ☑ Compounds with the general formula RCHO where –CHO is termed the aldehyde group. R may be H, alkyl or aryl group.

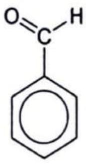
  Aliphatic aldehyde – R is an alkyl group; Aromatic aldehyde – R is an aryl group.

- ☑ Have at least one H atom attached to the carbonyl carbon atom.

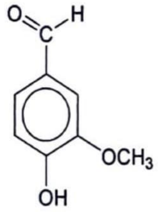
- ☑ Compounds with the general formula RCOR'. R and R' may be an alkyl or aryl group.

- ☑ Have two alkyl or aryl groups attached to the carbonyl carbon atom.

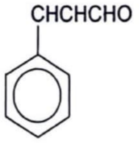
1.2 Examples of Naturally Occurring Carbonyl Compounds



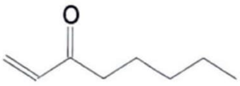
benzaldehyde
(bitter almond oil extract)



vanillin
(Vanilla flavouring)



cinnamaldehyde
or 3-phenylpropenal
(in cinnamon)



Oct-1-en-3-one
(in cooked mushrooms)

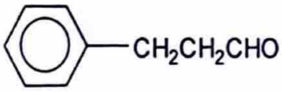
2 NOMENCLATURE

Aldehydes

For aliphatic aldehydes,

☐ the longest chain carrying the –CHO group is considered the parent structure and is named by replacing the *–e* of the corresponding alkane by *–al*.

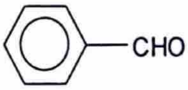
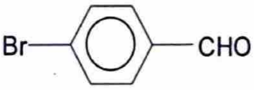
☐ the position of a substituent is indicated by a number, the carbonyl carbon being considered as carbon-1.

Structural Formula	IUPAC Name	Common Name
$HCHO$	methanal	formaldehyde
CH_3CHO	ethanal	acetaldehyde
CH_3CH_2CHO	propanal	
$CH_3(CH_2)_2CHO$	butanal	
	3–phenylpropanal	

For aromatic aldehydes,

☐ the parent structure is named as a *benzaldehyde*.

☐ the carbon on the benzene ring bearing the carbonyl functional group is considered carbon-1, and the position of a substituent on the benzene ring takes reference from this carbon-1.

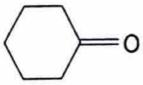
Structural Formula	IUPAC Name	Common Name
	benzaldehyde	benzenecarbaldehyde
	4–bromobenzaldehyde	

Ketones

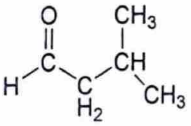
For ketones,

☐ the name is obtained by replacing the final *–e* of the name of the corresponding alkane with *–one*.

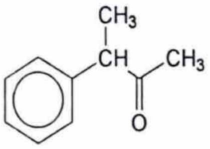
☐ the chain is numbered such that the carbonyl carbon atom has the lower possible number, and this number is used to designate its position.

Structural Formula	IUPAC Name	Common Name
CH_3COCH_3	propanone	acetone
$CH_3CH_2COCH_3$	butanone	
$CH_3CH_2CH_2COCH_3$	pentan–2–one	
$CH_3CH_2COCH_2CH_3$	pentan–3–one	
	cyclohexanone	

Practice: Name the following compounds



3-methylbutanal



3-phenylbutanone

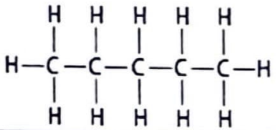
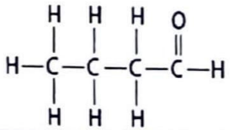
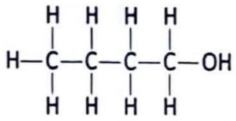
3 PHYSICAL PROPERTIES

3.1 Boiling points

As polar compounds, aldehydes and ketones have higher boiling points than alkanes of similar electron cloud size.

Example:

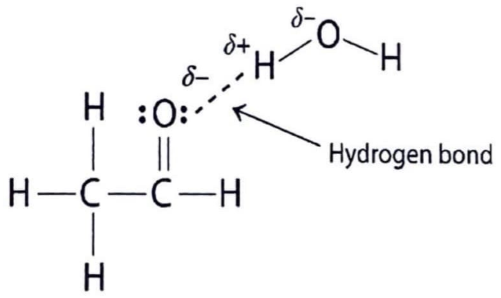
Table 1

	pentane	butanal	butan-1-ol
Structural formula			
Boiling point (°C)	36.0	76.0	117.2
M_r	72.0	72.0	74.0

Butan-1-ol has the highest boiling point as the hydrogen bonds are stronger and require more energy to break compared to permanent dipole-permanent dipole forces between butanal molecules and instantaneous dipole-induced dipole forces between pentane molecules.

Butanal has a higher boiling point than pentane as the permanent dipole-permanent dipole forces are stronger and require more energy to break than the instantaneous dipole-induced dipole forces between pentane molecules.

3.2 Solubility



The lone pair of electrons on the carbonyl oxygen atom allows carbonyl compounds to form hydrogen bonds with the H atom of water molecule. This ability to form hydrogen bonds accounts for the appreciable solubility of short-chain carbonyl compounds in water. As the length of the carbon chain increases, solubility in water decreases due to the increasing size of the non-polar alkyl chain. As the carbon chain length becomes longer (more than 5 carbons), the molecule has a larger non-polar hydrophobic hydrocarbon portion; the instantaneous dipole-induced dipole interactions become the predominant intermolecular forces.

Carbonyl compounds have good solubility in non-polar solvents. In fact, propanone, also known as acetone, is widely used as an organic solvent for cleaning apparatus in laboratories and is the active ingredient in nail polish remover.

4 PREPARATION METHODS FOR CARBONYL COMPOUNDS

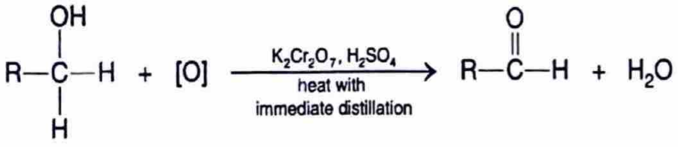
4.1 Oxidation of alcohols

☑ Candidates should be able to describe the formation of aldehydes and ketones from primary and secondary alcohols respectively.

The type of oxidation products obtained depends on the type of alcohol and the strength of the oxidising agent.

For example:

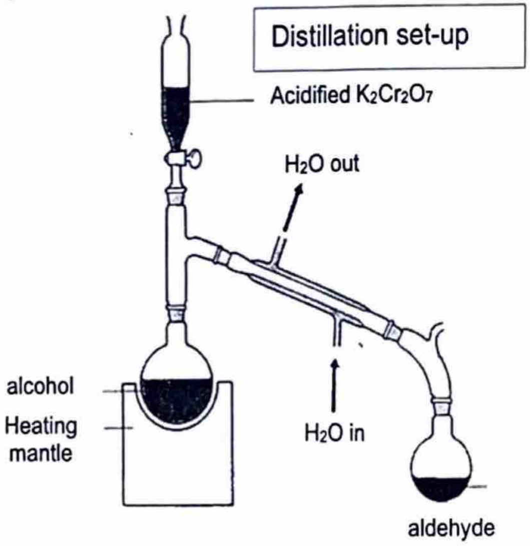
Oxidation of primary alcohol to form aldehyde



$$R-\underset{H}{\overset{OH}{C}}-H + [O] \xrightarrow[\text{heat with immediate distillation}]{K_2Cr_2O_7,\ H_2SO_4} R-\overset{O}{\overset{\|}{C}}-H + H_2O$$

Reagents:	$K_2Cr_2O_7$(aq), H_2SO_4(aq)
Conditions:	Heat with immediate distillation
Observations:	Orange solution turns green

Distillation set-up



☑ The oxidising agent is added slowly to the alcohol so that the alcohol is always in excess to prevent any unreacted oxidising agent from further oxidising the aldehyde to carboxylic acid.

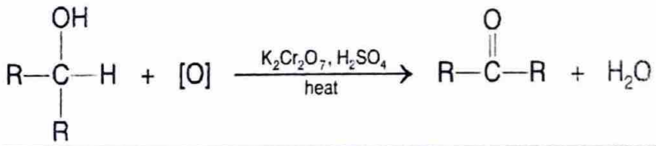
☑ $KMnO_4$ is too strong an oxidising agent to be used for this purpose.

☑ The reaction mixture is kept at a temperature below the boiling point of the alcohol and above that of the aldehyde so that the aldehyde is distilled off from the reaction mixture as it is formed.

☑ Immediate distillation of the aldehyde from the reaction will prevent further oxidation by the potassium dichromate(VI) in the flask. This is possible as the aldehyde has a lower boiling point than the alcohol.

Reason:
Aldehydes have weaker permanent dipole-permanent dipole forces between their molecules as compared to the hydrogen bonds between the alcohol molecules. Thus, less energy is required to break the permanent dipole-permanent dipole forces between the aldehyde molecules resulting in a lower boiling point of the aldehyde.

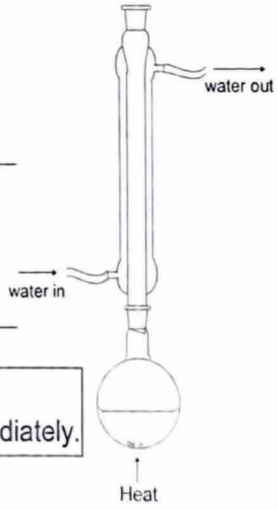
Oxidation of secondary alcohol to form ketone



$$R-\underset{R}{\overset{OH}{C}}-H + [O] \xrightarrow[\text{heat}]{K_2Cr_2O_7,\ H_2SO_4} R-\overset{O}{\overset{\|}{C}}-R + H_2O$$

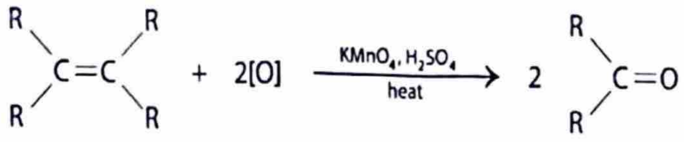
Reagent and conditions:	$K_2Cr_2O_7$(aq), H_2SO_4(aq), heat (or heat with reflux) or $KMnO_4$(aq), H_2SO_4(aq), heat (or heat with reflux)
Observations:	Orange solution turns green (for acidified $K_2Cr_2O_7$) Purple solution decolourises (for acidified $KMnO_4$)

Heat with reflux set-up



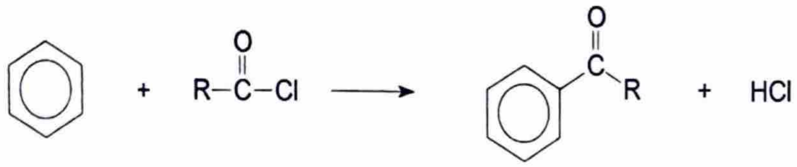
Q: Why is there no need to distil out the ketone immediately?
A: Ketones are not further oxidised by $K_2Cr_2O_7$ hence need not be distilled out immediately.

4.2 Oxidation of alkenes



Reagents and conditions:	$KMnO_4(aq)$, $H_2SO_4(aq)$, heat (or heat with reflux)
Observations:	Purple solution decolourises

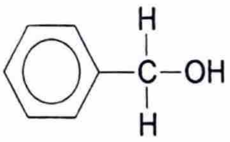
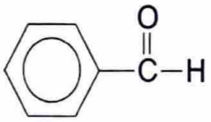
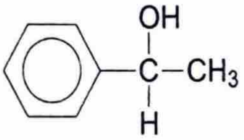
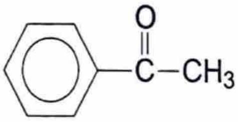
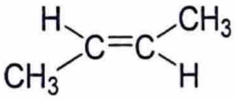
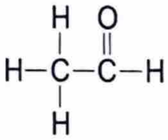
4.3 Electrophilic substitution of benzene (Friedel-Crafts acylation)



Reagents and conditions:	$RCOCl$, $AlCl_3$, room temperature (anhydrous)

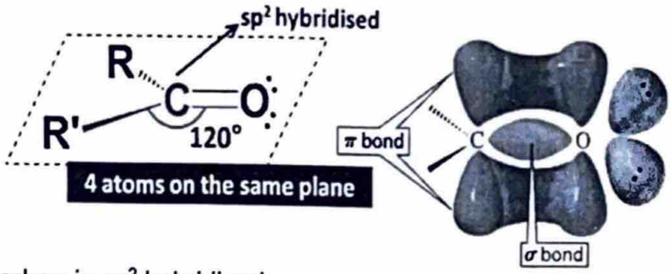
Exercise 1

Which of the following is correct?

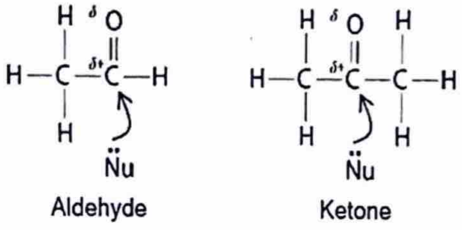
	Reactant	Reagent and conditions	Product
✓ 1		$K_2Cr_2O_7$, dilute H_2SO_4, heat with immediate distillation	
✓ 2		$K_2Cr_2O_7$, dilute H_2SO_4, heat (or heat with reflux)	
✗ 3		$KMnO_4$, dilute H_2SO_4, heat (or heat with reflux)	

5 CHEMICAL PROPERTIES OF CARBONYL COMPOUNDS

Structure and bonding



- The carbonyl carbon is *sp*sp^2 hybridised.
- The three sp^2 hybrid orbitals of this carbon form σ bonds with three other atoms.
- σ bonds are 120° apart (trigonal planar).
- The remaining *p*-orbital of C overlaps with a *p*-orbital of O to form a π-bond. The carbon and oxygen atoms are thus joined by a double bond.



Carbonyl compounds undergo **nucleophilic addition reactions.** A typical nucleophilic addition reaction is the addition of HCN molecule to the carbonyl functional group. (Refer to section 5.2)

Why do carbonyl compounds attract nucleophiles?	Why do carbonyl compounds undergo addition reactions?
• The C atom, of the –C=O group, i.e. the carbonyl carbon bears the partial positive charge as it is bonded to a more electonegative oxygen atom. • As a result, electron rich nucleophiles are attracted to this electron-deficient site.	• There is a C=O bond that is unsaturated.

5.1 Relative reactivity of carbonyl compounds towards nucleophilic attack

The susceptibility of the carbonyl carbon to nucleophilic attack is affected by the following factors:

(1) Electronic factor

Substituents on carbonyl carbon donate or withdraw electrons through inductive and / or resonance effects.

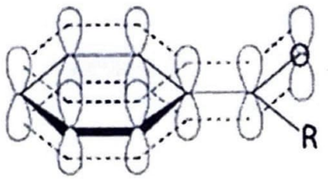
(a) Inductive effect

An inductive effect is the donation or withdrawal of electrons through σ bonds due to the electronegativity difference between atoms. Alkyl groups are electron-donating by inductive effect, which reduce the magnitude of the partial positive charge on the carbonyl carbon, and hence decrease attraction for nucleophiles and the susceptibility of the carbonyl carbon to nucleophilic attack.

If the substituent is electron donating, the carbonyl carbon becomes less electron deficient.

(b) Resonance effect

A resonance effect is the donation or withdrawal of electrons through π bonds due to the continuous side-on p-orbital overlap of the substituent and the carbonyl carbon. Aryl groups are electron-donating by resonance. (Refer to Section 6)



(Scan the QR Code above and point your camera to the "Hiro" marker for an augmented reality view of the overlap of the p orbitals of the carbonyl group and that of benzene's π electron cloud)

(2) Steric factor

Bulky alkyl groups increase steric hindrance about the carbonyl carbon, hinder the approach of the attacking nucleophile and hence contribute to a reduction in reactivity.

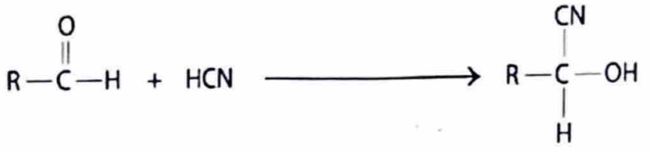
Conclusion:

From the two factors above, we can conclude that aldehydes are generally more reactive (towards nucleophiles) than ketones.

This is because:

- the carbonyl carbon in aldehydes is more electron deficient as it has only one electron-donating alkyl group while ketones have two such groups; and
- there is less steric hindrance around the carbonyl carbon in aldehydes as it is only bonded to one alkyl group.

5.2 Formation of cyanohydrins – Nucleophilic Addition

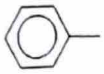


$$\mathrm{R-C(=O)-H + HCN \longrightarrow R-C(CN)(OH)-H}$$

aldehyde

cyanohydrin

R = alkyl group or



$$\mathrm{R-C(=O)-R + HCN \longrightarrow R-C(CN)(OH)-R}$$

ketone

cyanohydrin

Reagents and conditions: HCN, a trace amount of KCN

or HCN, a trace amount of KOH

or KCN, aq H_2SO_4

5.2.1 *Nucleophilic Addition Mechanism*

From kinetics studies of the nucleophilic addition of ethanal, the experimentally derived rate equation is:

$$\boxed{\text{rate} = k[\text{ethanal}][\text{CN}^-]}$$

This is consistent with the mechanisms shown on the next two pages whereby one ethanal molecule collides with one CN^- ion (nucleophile) in the slow step.

Generation of Nucleophile

HCN is a weak acid ($K_a = 5 \times 10^{-10}$ mol dm^{-3}) and only dissociates partially to give CN^-.

$$\mathrm{HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)}$$

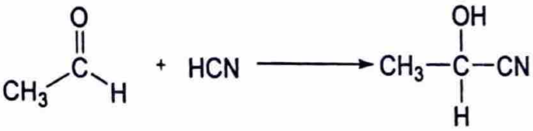
Since reaction rate is dependent on $[CN^-]$, a low $[CN^-]$ means a slow reaction.

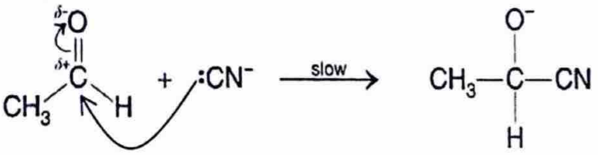
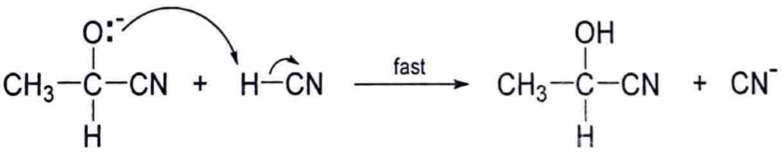
To increase the reaction rate, $[CN^-]$ can be increased through the use of:

(1) Addition of a strong electrolyte containing CN^- such as NaCN(aq) or KCN(aq)	$\mathrm{NaCN(aq) \longrightarrow Na^+(aq) + CN^-(aq)}$ $\mathrm{KCN(aq) \longrightarrow K^+(aq) + CN^-(aq)}$ • The complete ionisation of the electrolyte provides the initial CN^- ions for the nucleophilic attack on the carbonyl carbon.
(2) Addition of a small amount of strong base such as NaOH(aq) and KOH(aq)	• When a base such as OH^- is added, the H^+ ions are consumed to form water: $\mathrm{OH^- + H^+ \longrightarrow H_2O}$ • By Le Chatelier's Principle, the equilibrium position of $\mathrm{HCN \rightleftharpoons H^+ + CN^-}$ will shift to the right, resulting in an increase in the

	concentration of CN^-. Hence this provides the initial CN^- ions for the nucleophilic attack on the carbonyl carbon and the reaction rate increases. • The above reactions can be simplified to: $HCN + OH^- \longrightarrow H_2O + CN^-$

☑ Candidates should be able to describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones.



Reagents and conditions: HCN with trace amount of KCN Name of mechanism: Nucleophilic Addition Generation of Nucleophile: $KCN \longrightarrow K^+ + CN^-$	**Note:** KCN provides the initial CN^- ions for the nucleophilic attack on the carbonyl carbon.
Step 1: 	Step 1: The CN^- nucleophile attacks the electron-deficient carbonyl carbon atom. A lone pair of electrons from the CN^- nucleophile is used to form a bond with the carbonyl carbon. Simultaneously, the electron pair of the carbon-oxygen π bond shifts to the oxygen atom, giving an anionic tetrahedral intermediate (with a negative charge on the oxygen atom). The hybridisation of the carbon atom changes from sp^2 to sp^3.
Step 2:  Checklist for nucleophilic addition mechanism: ☐ Name of mechanism ☐ δ+ on C, δ– on O ☐ Lone pair of electrons on Nu ☐ Curly arrows to show flow of electrons - Lone pair on Nu to δ+ C - C=O bond to δ– O - Lone pair on O^- to H (of HCN) - H–C bond to C ☐ Label slow/fast steps	Step 2: The anionic intermediate is protonated to form the final cyanohydrin product. A proton can be abstracted from the undissociated HCN molecule (i.e. HCN acts as a Bronsted acid to protonate the anionic intermediate)

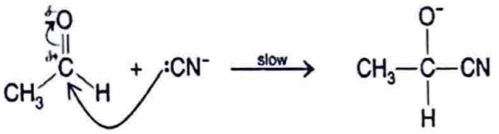
Reagents and conditions:
HCN with trace amount of KOH

Name of mechanism: Nucleophilic Addition

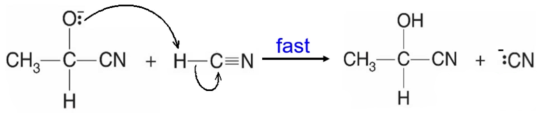
Generation of Nucleophile:

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

Step 1:



Step 2:



Checklist for nucleophilic addition mechanism:
- ☐ Name of mechanism
- ☐ δ+ on C, δ– on O
- ☐ Lone pair of electrons on Nu
- ☐ Curly arrows to show flow of electrons
  - Lone pair on Nu to δ+ C
  - C=O bond to δ– O
  - Lone pair on O⁻ to H (of HCN)
  - H–C bond to C
- ☐ Label slow/fast steps

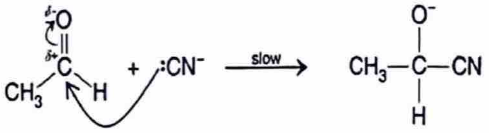
Reagents and conditions:
KCN, aq H_2SO_4

Name of mechanism: Nucleophilic Addition

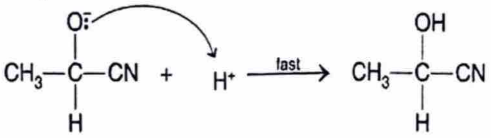
Generation of Nucleophile:

$KCN \longrightarrow K^+ + CN^-$

Step 1:



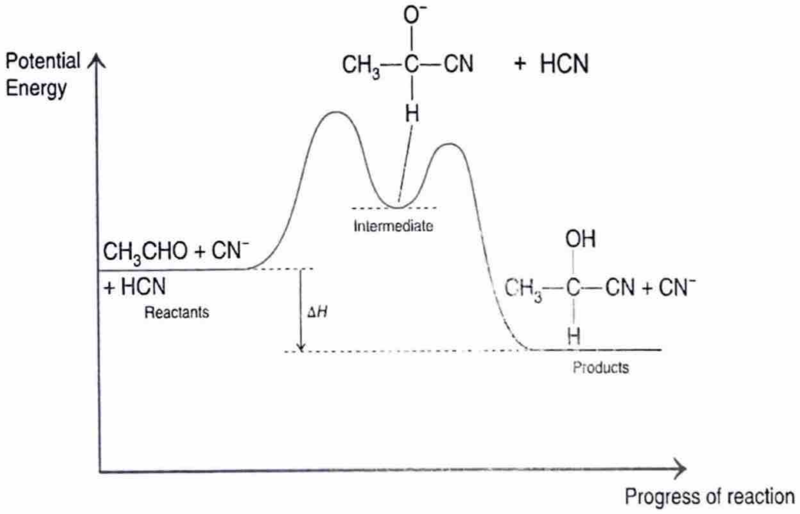
Step 2:



*(**Note:** In step 2, the H^+ ions comes from the acid dissociation of H_2SO_4.)*

Checklist for nucleophilic addition mechanism:
- ☐ Name of mechanism
- ☐ δ+ on C, δ– on O
- ☐ Lone pair of electrons on Nu
- ☐ Curly arrows to show flow of electrons
  - Lone pair on Nu to δ+ C
  - C=O bond to δ– O
  - Lone pair on O⁻ to H⁺
  - H–C bond to C
- ☐ Label slow/fast steps

The following energy profile diagram depicts the nucleophilic addition mechanism:



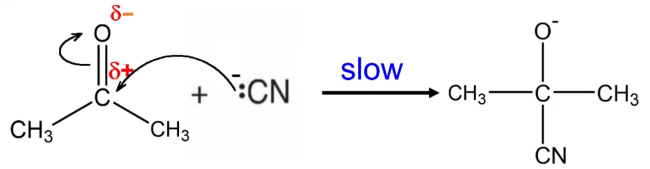
Exercise 2

Describe the mechanism for the reaction between propanone and HCN with trace amount of KOH to form the cyanohydrin, 2-hydroxy-2-methylpropanenitrile.

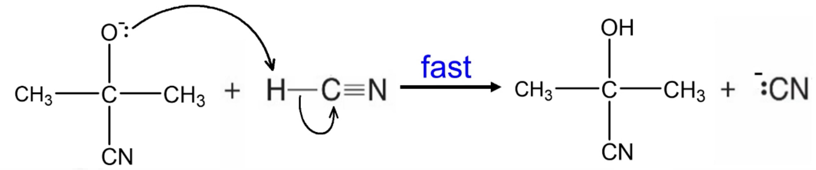
Name of mechanism: Nucleophilic addition

Generation of nucleophile: $HCN + OH^- \rightleftharpoons H_2O + CN^-$

Step 1: Nucleophilic attack by CN^- on the carbonyl carbon

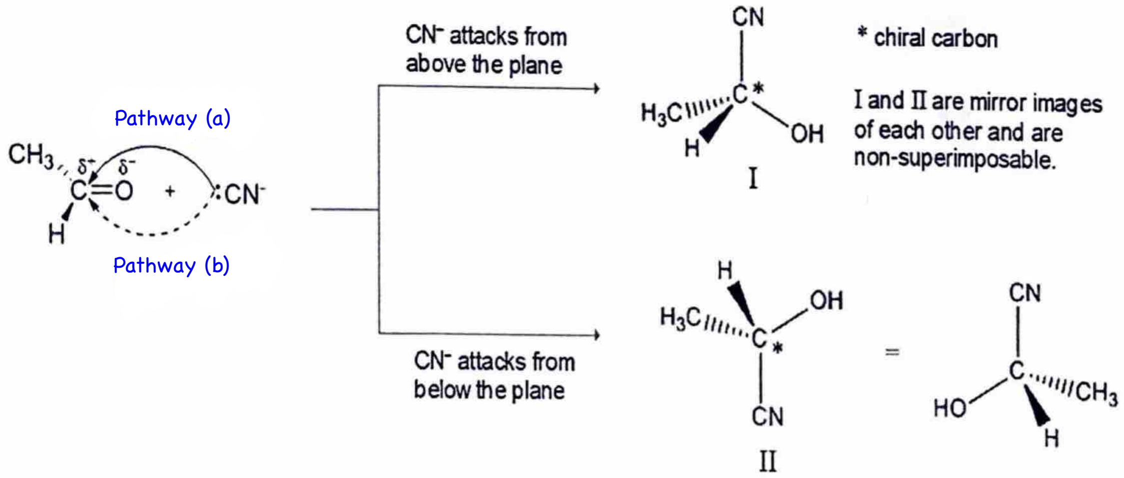


Step 2: Protonation of the anionic intermediate



5.2.2 *Stereochemistry of addition products*

Since the geometry around the *sp*² hybridised carbonyl carbon atom is trigonal planar, the nucleophile can attack the carbonyl carbon from either side of the plane with equal chance to form a racemic mixture (or racemate) containing equal proportions of the two enantiomers.



* chiral carbon

I and II are mirror images of each other and are non-superimposable.

(Scan the QR Code above to for an AR view of equal chance of nucleophilic addition from either side of the plane)

(Scan the QR Code above to for an AR view of both enantiomers for comparison)

☑ **Candidates should be able to explain the difference in reactivity between carbonyl compounds and alkenes towards nucleophilic reagents such as lithium aluminium hydride and hydrogen cyanide.**

5.2.3 Difference in reactivity between carbonyl compounds and alkenes towards nucleophiles

Why do carbonyl compounds undergo nucleophilic addition reactions but not alkenes?

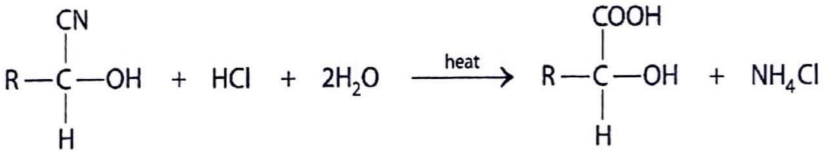
- The sp^2 hybridised C atom of the –C=O group, i.e. the carbonyl carbon, bears the partial positive charge as it is bonded to a more electonegative oxygen atom.
- As a result, electron rich nucleophiles, such as CN^-, are attracted to this electron-deficient site.
- The sp^2 hybridised C atoms of the C=C group in alkenes do not have a partial positive charge, and hence do not attract nucleophiles.

(Note: Both C=C and C=O π bonds are electron rich. Hence it is insufficient to state that the C=C π electron cloud repel the nucleophile CN^- as carbonyl with C=O group can undergo nucleophilic addition reaction).

5.3 Hydrolysis and reduction of cyanohydrins

Cyanohydrins are known also as 2-hydroxynitriles. Just like nitriles, cyanohydrins are useful reagents in organic synthesis as their formation extends the length of the carbon chain by one C atom. The difference is that there is an additional –OH group in the molecule. In addition, they serve as an intermediate in the synthesis of other organic compounds such as carboxylic acids and amines.

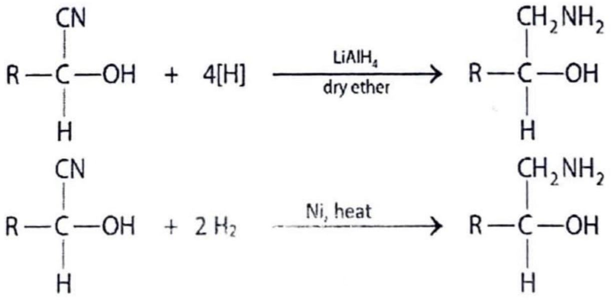
- Cyanohydrins can undergo acidic hydrolysis to form 2-hydroxycarboxylic acids.
  Note: Cyanohydrins do not undergo alkaline hydrolysis to yield the carboxylate salt.



$$\mathrm{R{-}\underset{H}{\overset{CN}{C}}{-}OH} + HCl + 2H_2O \xrightarrow{\text{heat}} \mathrm{R{-}\underset{H}{\overset{COOH}{C}}{-}OH} + NH_4Cl$$

Reagents and conditions: dilute $HCl(aq)$, heat
or dilute $H_2SO_4(aq)$, heat

- Cyanohydrins can undergo reduction, using different reagents, to form amines:



$$\mathrm{R{-}\underset{H}{\overset{CN}{C}}{-}OH} + 4[H] \xrightarrow[\text{dry ether}]{LiAlH_4} \mathrm{R{-}\underset{H}{\overset{CH_2NH_2}{C}}{-}OH}$$

$$\mathrm{R{-}\underset{H}{\overset{CN}{C}}{-}OH} + 2H_2 \xrightarrow{\text{Ni, heat}} \mathrm{R{-}\underset{H}{\overset{CH_2NH_2}{C}}{-}OH}$$

Reagents and conditions: $LiAlH_4$, dry ether
or H_2, Ni, heat
or H_2, Pt

Exercise 3 (J2003/1/30)

The product of the reaction between propanone and hydrogen cyanide is hydrolysed under acidic conditions. What is the formula of the final product?

A $CH_3CH(OH)CO_2H$

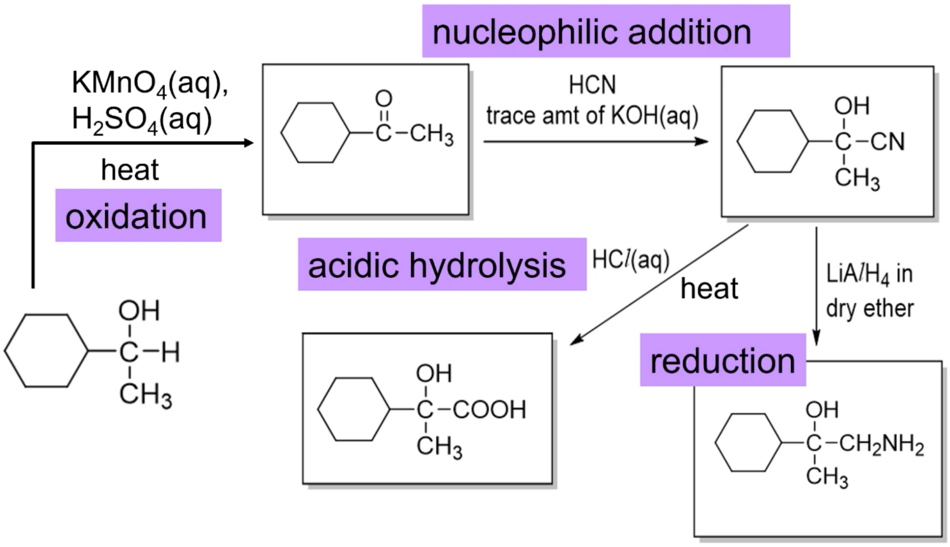
B $CH_3CH_2CH(OH)CO_2H$

C $CH_3CH_2CH_2CO_2H$

[✓ **D**] $(CH_3)_2C(OH)CO_2H$

Exercise 4

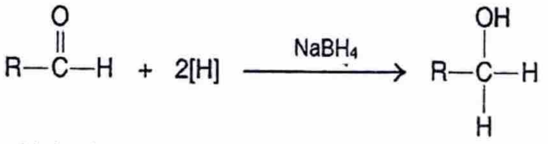
Fill in the blanks for the reaction scheme below.



5.4 Formation of alcohols – Reduction

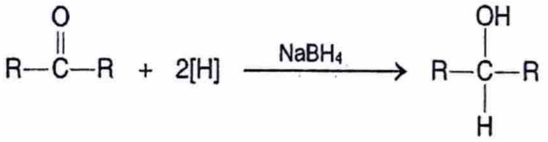
☑ Candidates should be able to describe the reduction of aldehydes and ketones to primary and secondary alcohols respectively.

Aldehydes are reduced to primary alcohols whereas ketones are reduced to secondary alcohols.



$$R-\overset{\overset{\large O}{\|}}{C}-H + 2[H] \xrightarrow{NaBH_4} R-\underset{\underset{\large H}{|}}{\overset{\overset{\large OH}{|}}{C}}-H$$

aldehyde primary alcohol



$$R-\overset{\overset{\large O}{\|}}{C}-R + 2[H] \xrightarrow{NaBH_4} R-\underset{\underset{\large H}{|}}{\overset{\overset{\large OH}{|}}{C}}-R$$

ketone secondary alcohol

Reagents and conditions:	$NaBH_4$ (specifically for carbonyl compounds) or $LiAlH_4$ in dry ether or H_2, Ni, heat

Any of the three reagents can be used to reduce the carbonyl compounds. The selection of a particular method over the others should factor in the reactivity, if any, of other functional groups present in the intended compound. For instance, if an organic compound contains both the aldehyde group and alkene functional groups, the use of H_2 with Ni and heat is not feasible unless the objective is to reduce both groups. If the objective is to only reduce the aldehyde group, use $NaBH_4$ instead.

Q: Can LiAlH$_4$ and NaBH$_4$ be used for reducing alkenes?

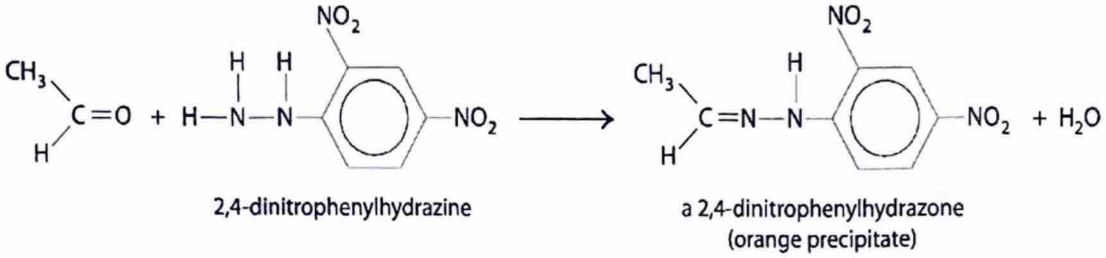
A: No. As LiAlH$_4$ and NaBH$_4$ are hydride sources, the reduction involves the H$^-$ nucleophile. Since the carbon atom of the C=C group in alkenes do not have a partial positive charge, it will be unable to attract the H$^-$ nucleophile, hence reduction will not occur.

5.5 Condensation reaction

☑ Candidates should be able to describe the use of 2,4–dinitrophenylhydrazine (2,4–DNPH) to detect the presence of carbonyl compounds.

Aldehydes and ketones react with the –NH$_2$ group of 2,4–dinitrophenylhydrazine (2,4-DNPH) to form 2,4–dinitrophenylhydrazones with the elimination of water.

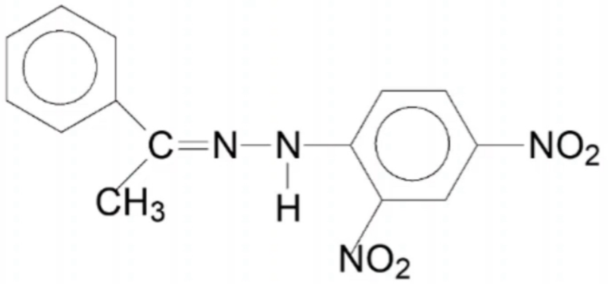
Dissolving solid 2,4-dinitrophenylhydrazine in methanol and some concentrated sulfuric acid gives Brady's reagent, which is used in the detection of carbonyl groups.



- The 2,4–dinitrophenylhydrazones formed are <u>orange crystalline solids</u>.
- Useful for the detection of aldehydes and ketones.
- Such reactions are termed condensation (or addition-elimination) reactions. A condensation reaction is one in which two molecules combine together with the elimination of a small molecule e.g. H$_2$O or NH$_3$. Note that the degree of unsaturation remains unchanged.

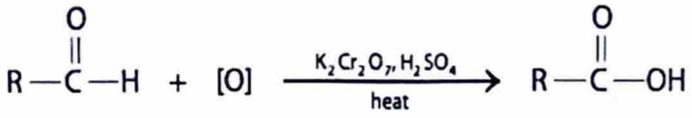
Exercise 5

Draw the structure of the product formed when C$_6$H$_5$COCH$_3$ reacts with 2,4-dinitrophenylhydrazine.



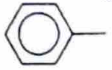
5.6 Formation of carboxylic acid – Oxidation (for aldehydes only)

☑ Candidates should be able to 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)



$$R-\overset{O}{\overset{\|}{C}}-H + [O] \xrightarrow[\text{heat}]{K_2Cr_2O_7, H_2SO_4} R-\overset{O}{\overset{\|}{C}}-OH$$

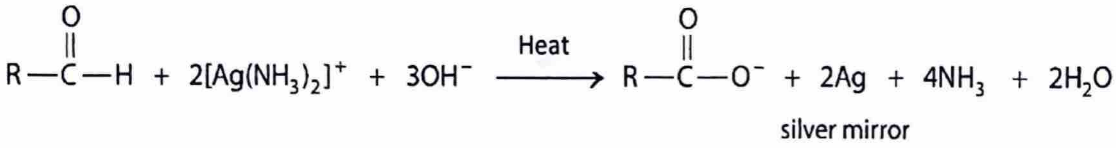
R = H or alkyl or



Reagents and conditons:	$K_2Cr_2O_7$(aq), H_2SO_4(aq), heat or $KMnO_4$(aq), H_2SO_4(aq), heat
Observations:	Orange $K_2Cr_2O_7$ turns green (using acidified $K_2Cr_2O_7$) Purple $KMnO_4$ turns colourless (using acidified $KMnO_4$)

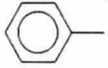
- Aldehydes are easily oxidised to carboxylic acids; ketones are not.
  (Note the exception that aromatic ketones can be further oxidised when heated with acidified $KMnO_4$ to form benzoic acid.)
- An aldehyde has a hydrogen atom attached to the carbonyl carbon, but not for ketones. Apparently, this hydrogen is abstracted in oxidation, either as a proton or an atom, and the analogous reaction for a ketone – abstraction of an alkyl or aryl group – does not take place.

5.7 Formation of carboxylate salts using Tollens' Reagent – Oxidation (for aldehydes only)



$$R-\overset{O}{\overset{\|}{C}}-H + 2[Ag(NH_3)_2]^+ + 3OH^- \xrightarrow{\text{Heat}} R-\overset{O}{\overset{\|}{C}}-O^- + \underset{\text{silver mirror}}{2Ag} + 4NH_3 + 2H_2O$$

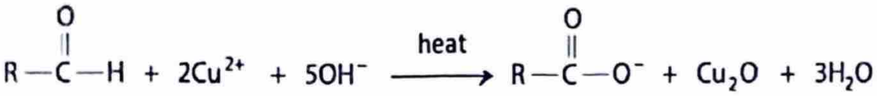
R = H or alkyl or



Reagents:	Tollens' reagent, (also referred to as alkaline diamminesilver(I) ions, $[Ag(NH_3)_2]^+$)
Conditions:	Heat
Observations:	A silver mirror is formed.

- Aldehydes (both aromatic and aliphatic) reduce the Ag(I) in Tollens' reagent to Ag. Under carefully controlled conditions, the silver will deposit on the walls of the reaction vessel as a mirror.
- Can be used to distinguish aldehydes from ketones since ketones do not react with Tollens' reagent.

5.8 Formation of carboxylate salts using Fehling's Solution – Oxidation of aliphatic aldehydes



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H + 2Cu^{2+} + 5OH^- \xrightarrow{\text{heat}} R-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + Cu_2O + 3H_2O$$

reddish-brown precipitate

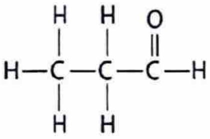
R = H or alkyl group only

Reagents and conditions:	Fehling's solution, heat or Benedict's solution, heat
Observations:	A brick-red ppt of Cu_2O is formed.

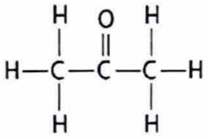
- *Fehling's solution*: Alkaline solution of Cu^{2+} ion complexed with tartrate ion.
- *Benedict's solution*: Alkaline solution of copper(II) citrate.
- Aliphatic aldehydes reduce the copper(II) in Fehling's/ Benedict's solutions to the brick-red copper(I) oxide, which is precipitated.
- Aromatic aldehydes and ketones do not react with Fehling's/ Benedict's solution. As such, this reaction can be used to tell apart an aliphatic aldehyde from the aromatic aldehydes and ketones compounds.

Exercise 6

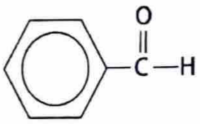
Determine the identity of liquids **A**, **B** and **C**, given that these are propanal, propanone and benzaldehyde but not necessary in the order.



Propanal



Propanone



Benzaldehyde

Since there are three colourless unknown compounds, at least two different tests need to be carried out to correctly identify them as shown below:

	Observations recorded for:		
	A	B	C
Test 1: Add Tollens' reagent to a sample of each compound and heat In a hot water bath	Silver mirror	No silver mirror	Silver mirror
Test 2: Add Fehling's solution to a fresh sample of each compound and heat In a hot water bath	Brick-red ppt	No brick-red ppt	No brick-red ppt
Deductions made:	Propanal	Propanone	Benzyldehyde

Exercise 7: N94/4/26

The compound C_3H_7Br undergoes a sequence of reactions as follows:

$$C_3H_7Br \xrightarrow{OH^-(aq)} X \xrightarrow{\text{Acidified } K_2Cr_2O_7} Y \xrightarrow{\text{Tollens' reagent}} Z + \text{silver mirror}$$

What could be the formulae for X, Y and Z?

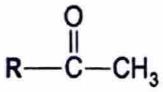
	X	Y	Z
A	$CH_3CH_2CH_2OH$	$CH_3CH_2CO_2H$	CH_3CH_2CHO
B	$CH_3CH{=}CH_2$	$CH_3CH(OH)CH_2OH$	$CH_3CH_2CO_2H$
C	$CH_3CH_2CH_2OH$	CH_3CH_2CHO	$CH_3CH_2CO_2H$
D	$CH_3CH(OH)CH_3$	CH_3COCH_3	CH_3CO_2H

5.9 Formation of tri-iodomethane (iodoform) – Oxidation (for carbonyl cpds with CH_3CO–)

(refer to hydroxy compounds lecture notes on compounds with $-CH(OH)CH_3$)

☑ Candidates should be able to describe the reaction of CH_3CO– compounds with alkaline aqueous iodine to give tri-iodomethane.

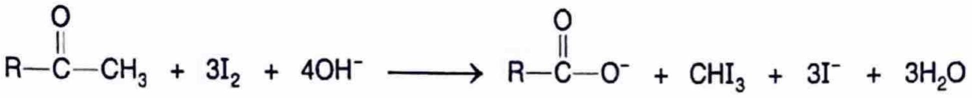
Only carbonyl compounds containing the following structure can undergo this oxidation reaction. This group of compounds consists of ethanal and all ketones containing $-COCH_3$ group.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

R must be either a H atom or an alkyl or aryl group.

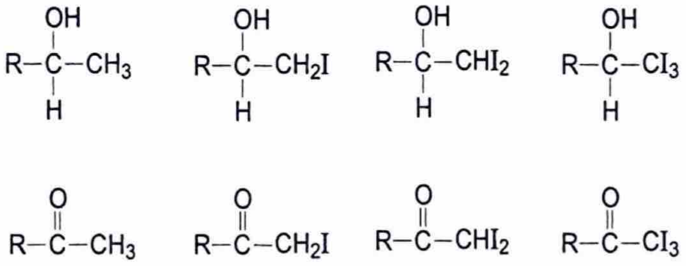
When such carbonyl compounds are heated with alkaline $I_2(aq)$, a carboxylate salt will be obtained along with yellow crystals of tri-iodomethane, CHI_3:



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + 3I_2 + 4OH^- \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + CHI_3 + 3I^- + 3H_2O$$

Reagents and conditions:	$I_2(aq)$ with NaOH(aq), heat or $I_2(aq)$ with KOH(aq), heat
Observations:	Yellow ppt of CHI_3

In general, alcohols, aldehydes and ketones with the following structures give positive results for tri-iodomethane test. (Refer to hydroxy compound lecture notes)



$$R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3 \quad R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_2I \quad R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CHI_2 \quad R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CI_3$$

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \quad R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2I \quad R-\overset{\overset{\displaystyle O}{\|}}{C}-CHI_2 \quad R-\overset{\overset{\displaystyle O}{\|}}{C}-CI_3$$

R must be either a H atom or an alkyl or aryl group.

Exercise 8

How many structural isomers, with the molecular formula $C_6H_{12}O$, can give yellow crystals of tri-iodomethane with hot alkaline aqueous iodine and orange precipitate with 2,4-dinitrophenylhydrazine?

A 1 B 2 C 3 D 4 D

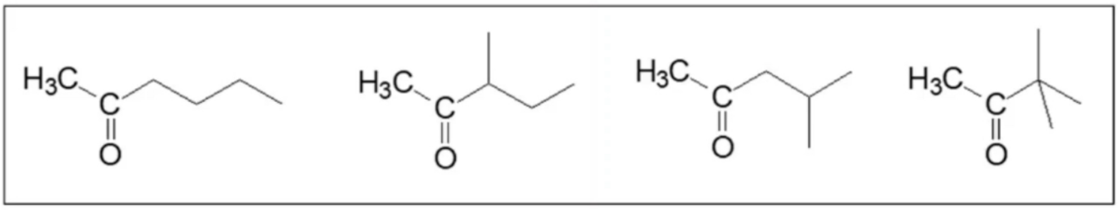
$C_6H_{12}O$ gives orange ppt. with 2,4-DNPH

$\Rightarrow$ $C_6H_{12}O$ is an aldehyde or ketone.

$C_6H_{12}O$ gives yellow CHI_3 with hot alkaline $I_2(aq)$

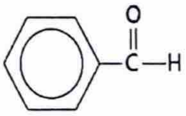
$\Rightarrow$ $C_6H_{12}O$ contains CH_3CO– structure.

Hence $C_6H_{12}O$ is a ketone with formula, **$CH_3COC_4H_9$**.

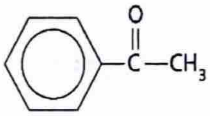


6 REACTIVITY OF AROMATIC CARBONYL COMPOUNDS

Benzaldehyde and phenylethanone are the simplest examples of aromatic carbonyl compounds.



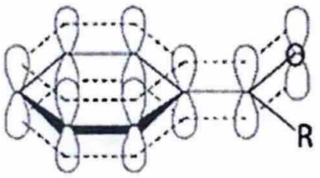
Benzaldehyde



Phenylethanone

Aromatic carbonyl compounds are generally <u>less reactive</u> towards nucleophilic attack as compared to their aliphatic counterparts.

The carbonyl C atom in an aromatic carbonyl compound is <u>less electron-deficient</u> due to the interaction of the π electron cloud of the carbonyl group and those of the adjacent benzene ring.



Being derivatives of benzene, these compounds can also undergo electrophilic substitution reactions whereby the carbonyl group is considered to be ring deactivating and 3-directing (refer to Arenes lecture notes).

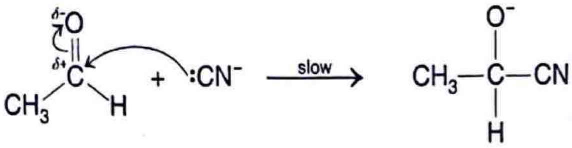
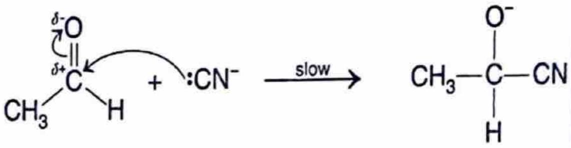
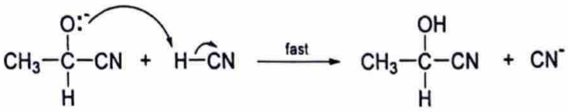
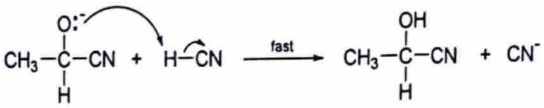
7 SUMMARY OF REACTIONS WITH OXIDISING AND REDUCING AGENTS

Oxidising agents	Functional Groups and Products	Reducing agents	Functional Groups and Products
$KMnO_4$, dilute H_2SO_4, heat	• Alkenes → CO_2, carboxylic acid or ketone (oxidative cleavage) • Alkylbenzenes→benzoic acid • 1° alcohols → carboxylic acid • 2° alcohols → ketone • Aldehydes → carboxylic acid	H_2, Ni, Heat (or H_2, Pt)	• Alkenes → alkane • Aldehydes → 1° alcohol • Ketones → 2° alcohol • Nitrile: $RC{\equiv}N \rightarrow RCH_2NH_2$
$K_2Cr_2O_7$, dilute H_2SO_4, heat	• 1° alcohols → aldehyde (immediate distillation) • 2° alcohols → ketone • Aldehydes →carboxylic acid	$LiAlH_4$ in dry ether	• Aldehydes → 1° alcohol Ketones → 2° alcohol • Nitrile: $RC{\equiv}N \rightarrow RCH_2NH_2$ • Carboxylic acids→ 1° alcohol • Amides → amine (refer to Organic Nitrogen Compounds)
Tollens' reagent $[Ag(NH_3)_2]^+$, heat	All aldehydes → carboxylate or benzoate salt	$NaBH_4$ (specific for carbonyls)	Aldehydes → 1° alcohol Ketones → 2° alcohol
Fehling's solution (Alkaline copper(II) tartrate)	Aliphatic aldehydes → carboxylate salt		

8 SUMMARY OF DISTINGUISHING TESTS

To distinguish:	Reagents and Conditions	Expected Observation
Carbonyl compounds from other functional groups	2,4–dinitrophenylhydrazine (2,4-DNPH)	Carbonyl compounds will give an orange ppt.
Between aldehydes and ketones	$KMnO_4(aq)$ / dil. H_2SO_4 and heat	Aldehydes will decolourise the purple $KMnO_4$. (Note the exception that aromatic ketones can be further oxidised when heated with acidified $KMnO_4$ to form benzoic acid.)
	$K_2Cr_2O_7(aq)$ / dil. H_2SO_4 and heat	Aldehydes will change the solution from orange to green.
	Tollens' reagent, heat	Aldehydes will give a silver mirror.
	Fehling's solution, heat	Aldehydes will give brick-red ppt of Cu_2O. (only for aliphatic aldehydes)
Between aliphatic and aromatic aldehydes	Fehling's solution, heat	Aliphatic aldehydes will give brick-red ppt of Cu_2O.
Compounds with $-COCH_3$ group	Alkaline aqueous I_2, heat	Compounds with $-COCH_3$ group will give yellow ppt of CHI_3.

9 SUMMARY OF NUCLEOPHILIC ADDITION MECHANISM

1. Using HCN with trace/small amount of KCN	2. Using HCN with trace/small amount of KOH
Name of mechanism: Nucleophilic Addition	**Name of mechanism:** Nucleophilic Addition
Generation of nucleophile: $KCN \longrightarrow K^+ + CN^-$	**Generation of nucleophile:** $OH^- + HCN \longrightarrow H_2O + CN^-$ Please note the difference in this step
Step 1: 	**Step 1:** 
Step 2: 	**Step 2:** 

Checklist for nucleophilic addition mechanism:

- ☐ Name of mechanism
- ☐ δ+ on C, δ– on O
- ☐ Lone pair of electrons on Nu
- ☐ Curly arrows to show flow of electrons
  - Lone pair on Nu to δ+ C
  - C=O bond to δ– O
  - Lone pair on O⁻ to H (of HCN)
  - H–C bond to C
- ☐ Label slow/fast steps

10 SUMMARY OF METHODS TO EXTEND/SHORTEN THE CARBON CHAIN

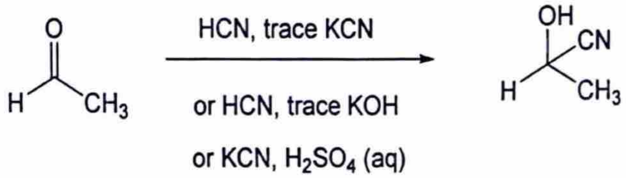
To **extend** the carbon chain:

1. **Halogenoalkane** with ethanolic KCN, heat (or heat under reflux)

Example $CH_3CH_2Br \xrightarrow[\text{heat}]{\text{ethanolic KCN}} CH_3CH_2CN$

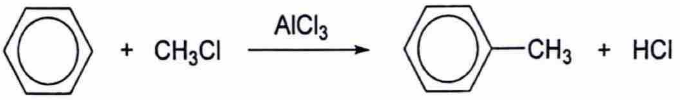
2. **Ketone/Aldehyde** with HCN, trace KCN, cold

Example

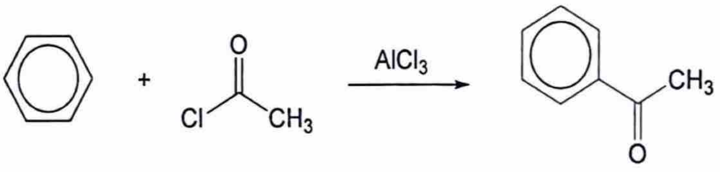


3. **Friedel-Crafts alkylation or acylation** (only for compounds with aryl groups)

Example



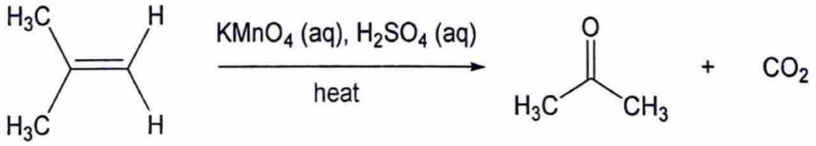
Example



To **shorten** the carbon chain:

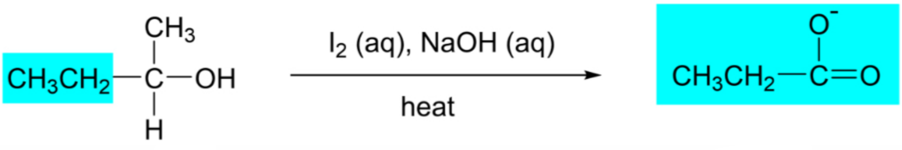
1. **Alkene** with acidified KMnO4, heat (or heat under reflux)

Example



2. Structures that can undergo tri-iodomethane (oxidation) reaction

Example



$$CH_3CH_2-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large H}{|}}{C}}-OH \xrightarrow[\text{heat}]{I_2\text{ (aq), NaOH (aq)}} CH_3CH_2-\overset{\overset{\large O^-}{|}}{C}{=}O$$

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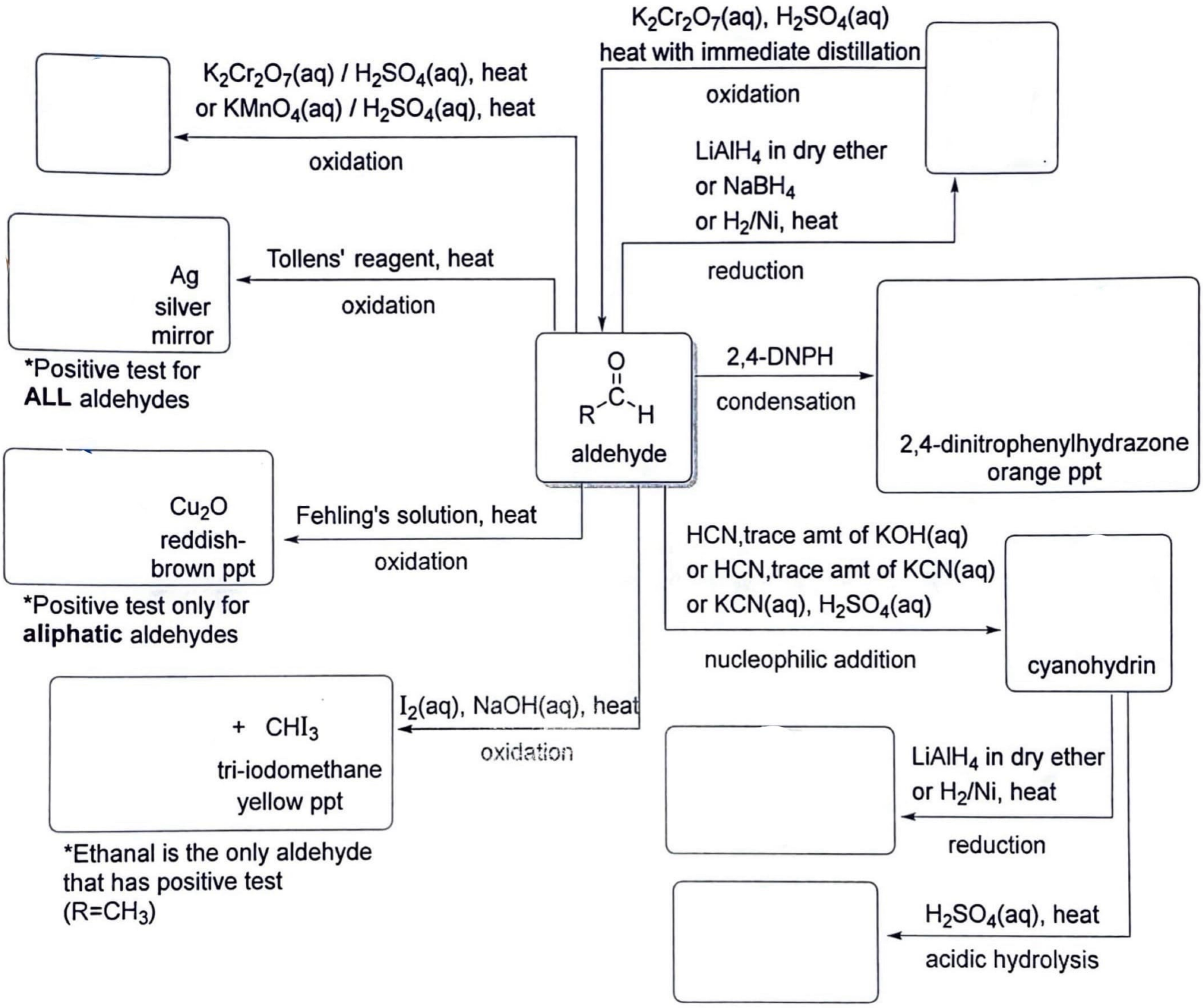
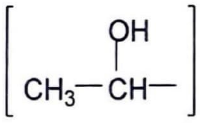
YEAR 6 H2 CHEMISTRY 2023
Tutorial 17: Carbonyl Compounds

Reaction Mindmaps

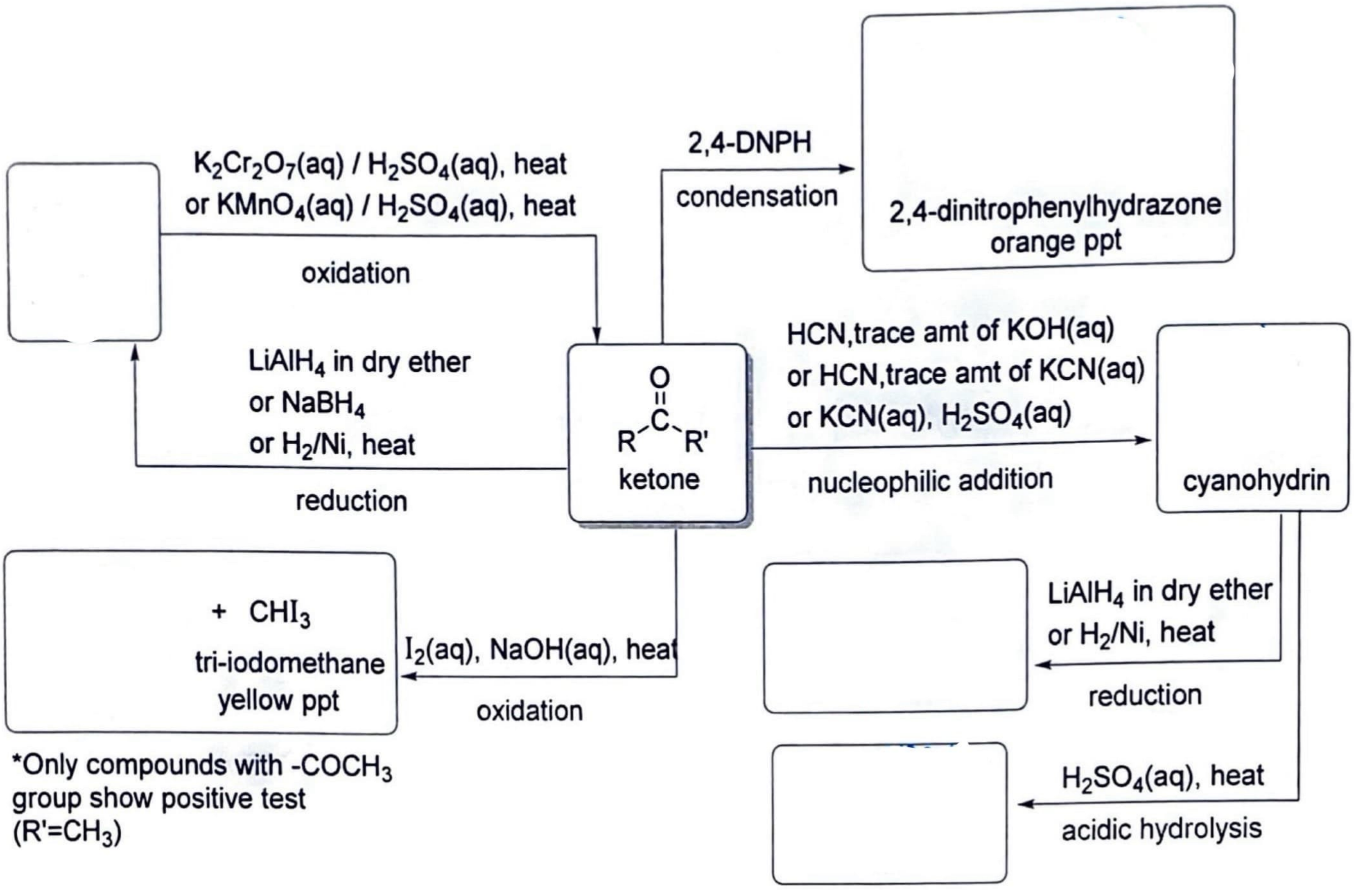
Fill in the blanks below.

☐ Aldehydes



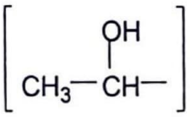
Note: Alcohols with  $\left[CH_3-\overset{OH}{\overset{|}{C}}H-\right]$ also give yellow ppt of CHI_3 when heated with $I_2(aq)$ and NaOH(aq)

❑ Ketones



*Only compounds with -COCH$_3$ group show positive test (R'=CH$_3$)

Notes:

1) Alcohols with  $\left[CH_3-\overset{OH}{\overset{|}{CH}}- \right]$ also give yellow ppt of CHI$_3$ when heated with I$_2$(aq) and NaOH(aq)

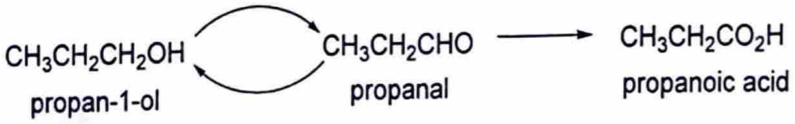
2) Aliphatic ketones generally do not undergo oxidation with Tollens' reagent, Fehling's solution, hot acidified K$_2$Cr$_2$O$_7$ and hot acidified KMnO$_4$.

Self-check Questions

1 Write down the structural formula for each of the following compounds:

- **(a)** pentan-3-one
- **(b)** 3-methylhexanal
- **(c)** cyclohexanone
- **(d)** trans-but-2-enal
- **(e)** 4-hydroxybenzaldehyde

2 The Harcourt and Esson reaction is a redox reaction. This type of reaction also occurs in organic chemistry, as the following transformation show.



(a) State the reagents and conditions you could use to convert propanal into propan-1-ol.

(b) Both propanal and propanoic acid can be obtained from propan-1-ol. State the reagents you could use to carry out these reactions. How would you ensure that the main product was propanal rather than propanoic acid?

(c) Draw the structure of the product formed when 2,4-dinitrophenylhydrazine is added to propanal. State the expected observations.

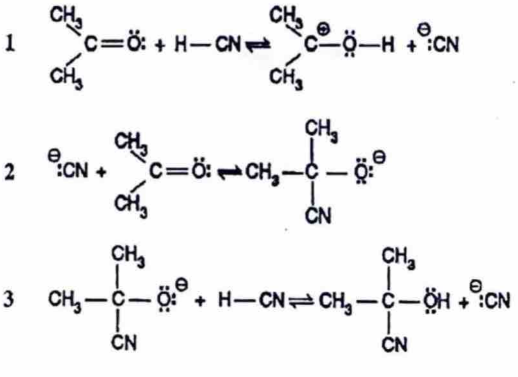
[modified from N13/3/5(e)]

3. For which one of the following can a solution of iodine in aqueous sodium hydroxide be used to distinguish between members of the pair?

- A CH_3CHO and CH_3COCH_3
- B CH_3CH_2CHO and CH_3COCH_3
- C CH_3CH_2OH and $CH_3CH_2CH(OH)CH_3$
- D CH_3OH and CH_3CH_2CHO

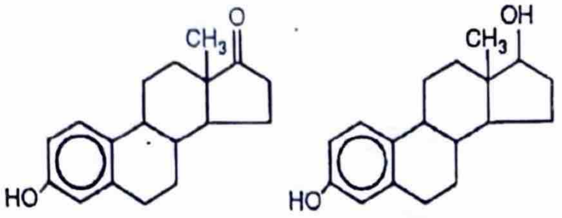
4. Hydrogen cyanide adds to propanone most readily under mildly alkaline conditions.

Which of the following are steps in the addition reaction?



- A 2 only
- B 1 and 2 only
- C 2 and 3 only
- D 1, 2 and 3

5. Two female sex hormones are oestrone and oestradiol.



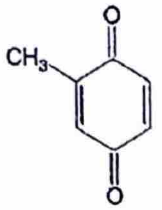
oestrone oestradiol

Which of the following reagents could be used to distinguish between the two hormones?

A $Br_2(aq)$ at room temperature
B 2,4-dinitrophenylhydrazine
C Fehling's or Tollens' reagent
D I_2 in NaOH(aq)
E sodium

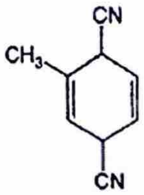
N91/I/29; J2000/III/24

7. The unsaturated diketone shown is excreted by the bombardier beetle.

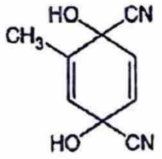


What is formed when this compound reacts with hydrogen cyanide?

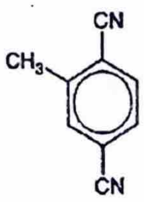
A



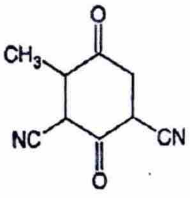
B



C

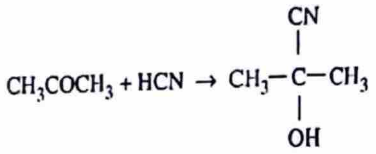


D



N2000/III/26

6. The following reaction is an intermediate stage in the manufacture of the important polymer known as *Perspex*.



$$CH_3COCH_3 + HCN \rightarrow CH_3-\underset{\displaystyle OH}{\overset{\displaystyle CN}{C}}-CH_3$$

What type of mechanism is involved in this reaction?

A electrophilic addition
B electrophilic substitution
C free radical substitution
D nucleophilic addition

Practice Questions

1 Cyanohydrins are useful intermediates in organic synthesis. They can be made by reacting aldehydes and ketones with a solution of HCN to which a small amount of NaCN has been added.

(a) **(i)** Describe the mechanism of the reaction between hydrogen cyanide and ethanal, CH_3CHO, to form 2-hydroxypropanenitrile, $CH_3CH(OH)CN$.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.

(ii) State the roles of HCN and NaCN in the mechanism of this reaction.

(iii) Explain why propanone reacts at a slower rate than ethanal.

(b) The product of the reaction in **(a)(i)** forms lactic acid when heated with dilute sulfuric acid. Draw the structure of lactic acid and state the type of reaction involved.

(c) Lactic acid present in milk rotates the plane of polarised light. Lactic acid produced in a laboratory by the above reactions does not rotate the plane of polarised light.

(i) What feature of the lactic acid present in milk causes the rotation of the plane of polarised light?

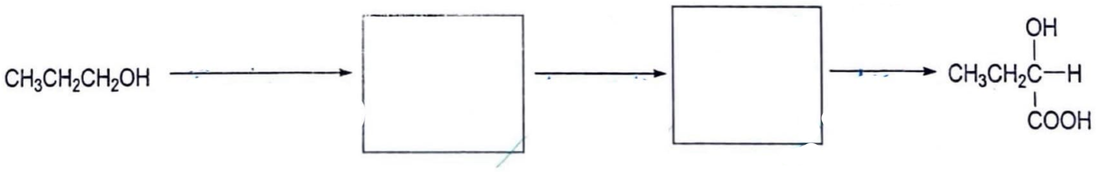
(ii) With reference to your mechanism in **(a)(i)**, and the shape of the CH_3CHO molecule, suggest why synthetic lactic acid does not rotate the plane of polarised light.

2 State the reagents and conditions needed for the following conversions. Draw the structure of the intermediate in each case.

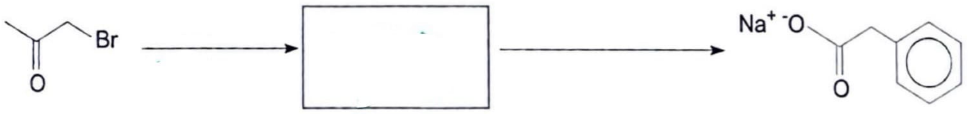
(a)

(b)

(c)



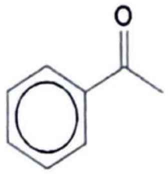
(d)



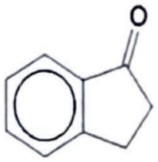
[modified from RI 2017 CT2 B2]

3 For each of the following pairs of compounds, describe one **simple** chemical test which would enable you to distinguish between them. State clearly how **each** compound behaves in the test.

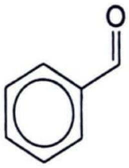
(a)



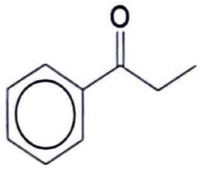
and



(b)



and



4 Identify the compounds **A** to **C** described below, giving reasons for your answer.

(a) **A** (C_8H_8O) gives an orange precipitate with 2,4-dinitrophenylhydrazine and silver mirror with Tollens' reagent but does not react with Fehling's solution. When heat with acidified $KMnO_4$, **A** forms 1,4-benzenedicarboxylic acid.

(b) **B** (C_3H_8O) on oxidation with hot acidified potassium manganate(VII) gives **C** (C_3H_6O). **C** gives an orange precipitate with 2,4-dinitrophenylhydrazine.

5 Compound **A** ($C_5H_{10}O$) is one of the volatile compounds isolated from white button mushrooms. Compound **A** gives an orange precipitate **B** with 2,4-dinitrophenylhydrazine. When compound **A** is heated with acidified potassium dichromate(VI), compound **C** ($C_5H_{10}O_2$) is obtained. When compound **A** is reacted with sodium borohydride, compound **D** is obtained. When compound **D** is heated with aluminium oxide, only compound **E** is obtained. Compound **E** reacts with hot, acidified potassium manganate(VII) to give only one organic compound, 2-methylpropanoic acid.

(a) Deduce the structures of compounds **A** to **E**, giving reasons for your answer.

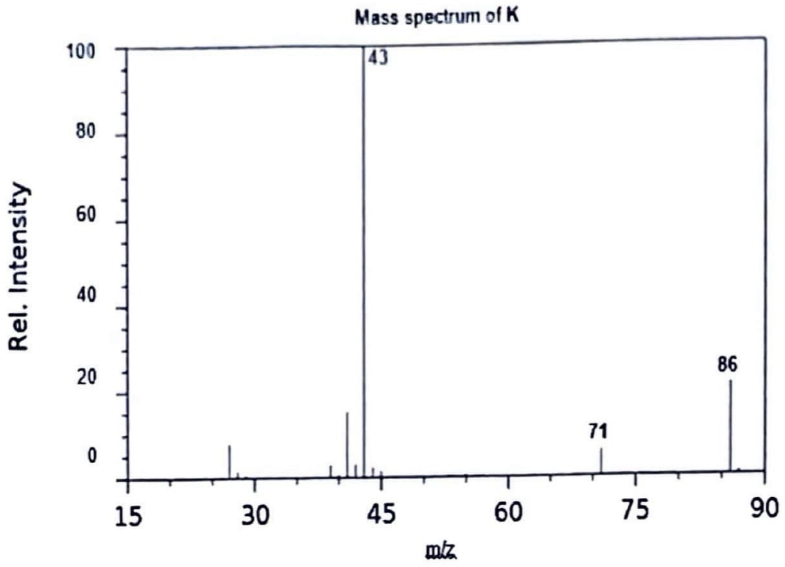
(b) Reduction of carbonyl compounds by lithium aluminium hydride and sodium borohydride proceed via nucleophilic addition.

Suggest why lithium aluminium hydride is a stronger reducing agent than sodium borohydride, given that both reducing agents produce hydride ions as the reacting species.

[modified 2017 P2 Q4(c)(iii)]

6 Mass spectrometry is an analytical technique that ionises chemical species into various molecular cationic fragments of the form, M^+. The largest m/z value corresponds to the molecular mass of the compound.

Compound **K** is analysed using a mass spectrometer. The mass spectrum of **K** is shown on the next page.



(a) Given that the largest m/z value corresponds to the molecular mass of **K**, $C_nH_{2n}O$, calculate the value of n.

An alcohol **J**, $C_nH_{2n+2}O$, undergoes oxidation to give **K**. **K** gives a yellow precipitate with alkaline $I_2(aq)$. When treated with hot aluminium oxide, **J** gives only two alkenes, both of which do not exhibit *cis-trans* isomerism.

(b) Suggest the structures of **J** and **K**, explaining your reasoning.

[modified from RI 2017 CT2 C2]

7 The simplest amide, methanamide, $HCONH_2$, can be dehydrated to hydrogen cyanide, HCN.

$$HCONH_2 \longrightarrow HCN + H_2O$$

In some circumstances, double bonds will undergo a nucleophilic addition reaction.

Suggest reasons to explain Fig. 1.
Use the concepts of electronegativity, electronic and steric effects, and delocalisation in your answer.

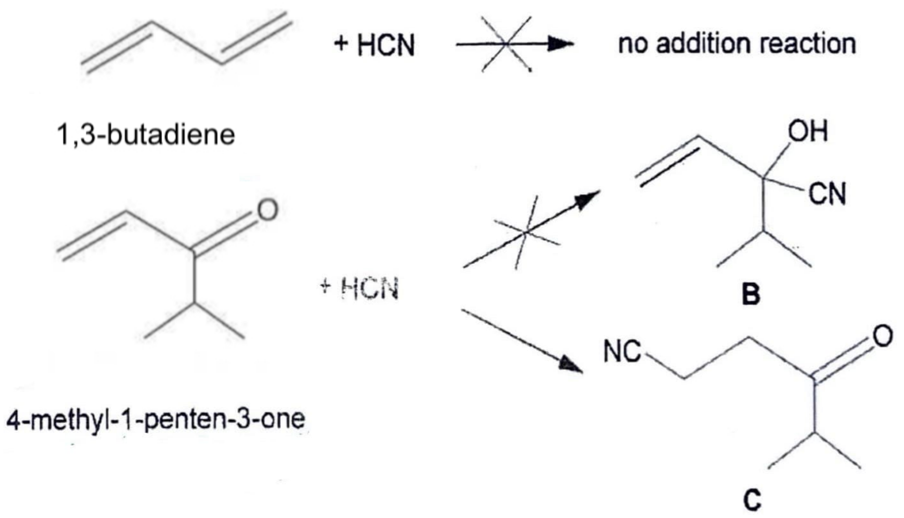


Fig. 1

[2018 P3 Q1(e)]