17 Extension Topic – Organic Chemistry Carbonyl Compounds

GUIDING QUESTIONS

- How are carbonyl compounds synthesized?
- Which class of reagents do carbonyl compounds react with and why? What types of reactions do carbonyl compounds undergo and why?
- How do carbonyl compounds react with HCN in nucleophilic addition?

LEARNING OUTCOMES

Students should be able to:

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

11.6(b) describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones

11.6(c) explain the differences in reactivity between carbonyl compounds and alkenes towards nucleophilic reagents, such as lithium aluminium hydride and hydrogen cyanide.

11.6(d) describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) to detect the presence of carbonyl compounds

11.6(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)

11.6(f) deduce the presence of a $CH_3CO–$ group from its reaction with alkaline aqueous iodine to give tri-iodomethane

REFERENCES

1. Peter Cann & Peter Hughes (2014). *Chemistry*, Hodder Education, Chapter 17
2. John McMurry (2012). *Organic Chemistry*. 9th Edition, Cengage Learning, Chapter 19

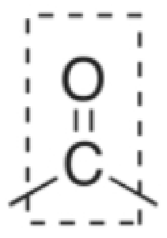
1 INTRODUCTION

Carbonyl compounds are commonly found in biologically important molecules such as carbohydrates and hormones, as well as other natural and synthetic dyes, fragrances and pharmaceuticals.

Hedione (methyl hydrojasmonate) was discovered in the early 1960s and is one ingredient found in almost all fine fragrances. During a quest to identify the characteristic smell of Bulgarian rose oil, the rose ketones, damascenones, were discovered and synthesized. In general, aldehydes contribute to the floral concept in feminine perfumery and aliphatic aldehydes with 8–13 carbon atoms have a very pleasant odour, and can be detected in very low concentrations.

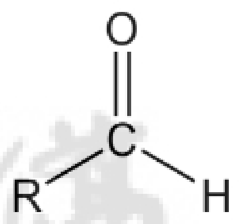
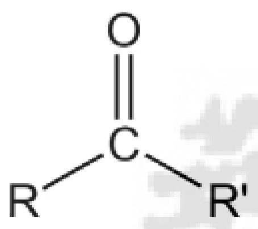
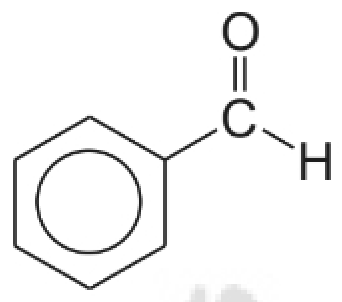
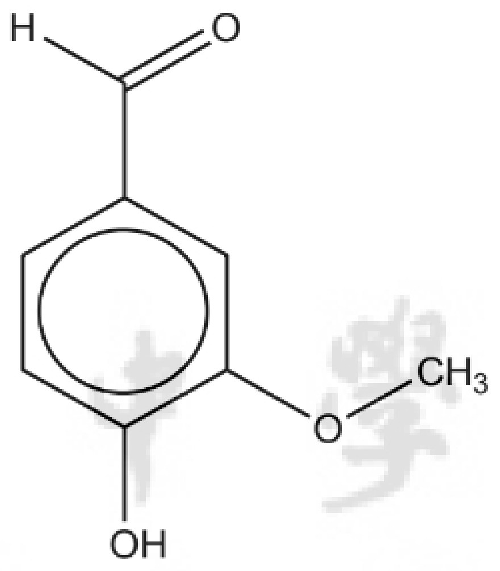
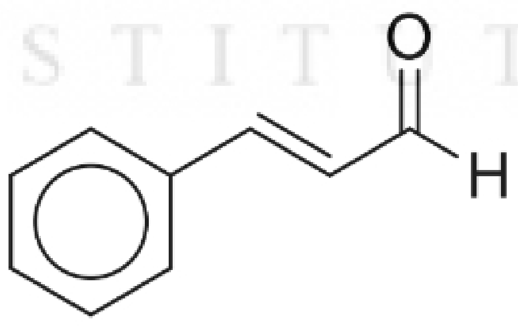
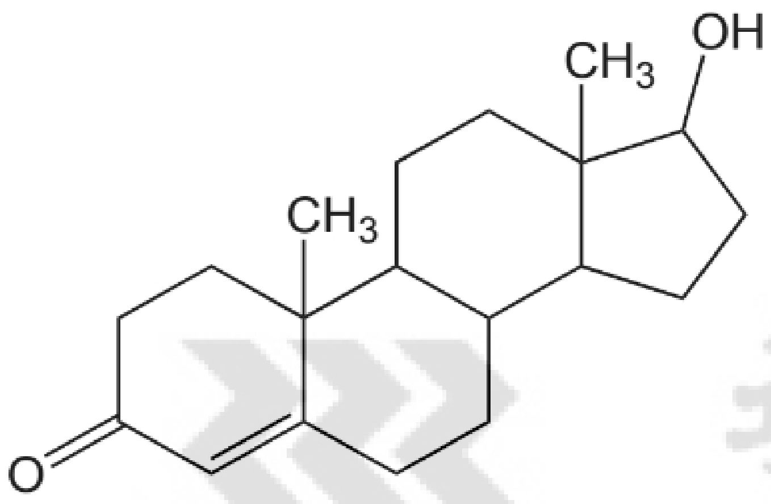
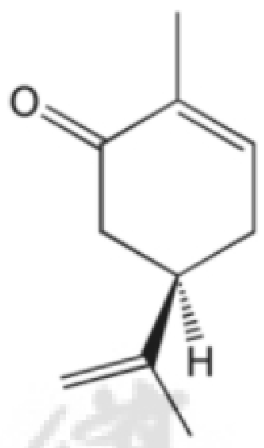
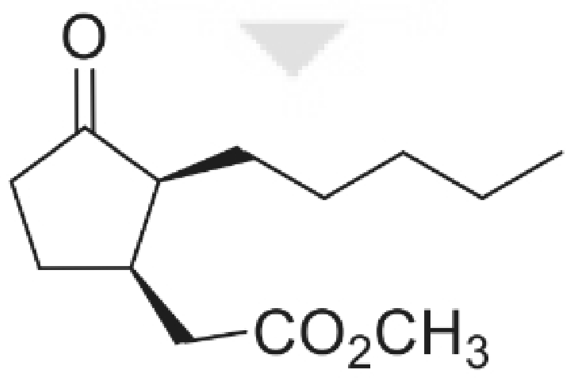
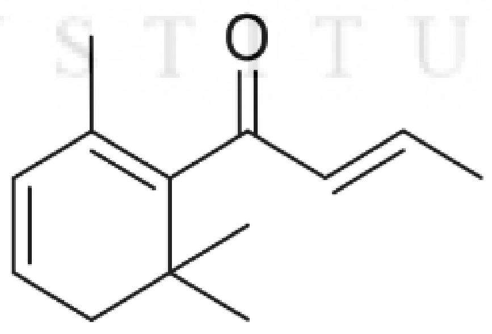
Benzaldehyde, the simplest aromatic aldehyde, has a pleasant almond-like odour, while cinnamaldehyde gives cinnamon note. Vanillin (4–hydroxyl–3–methylbenzaldehyde) is used as vanilla note, an ubiquitous note in almost all fragrances.

A carbonyl group is composed of a carbon atom which is double bonded to an oxygen atom.



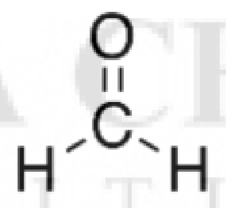
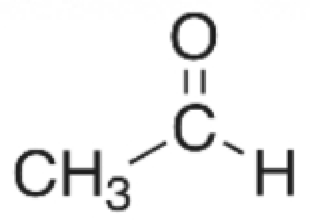
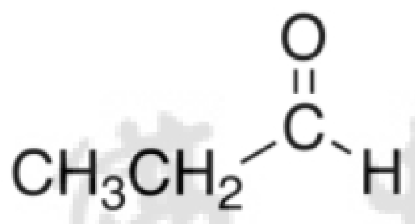
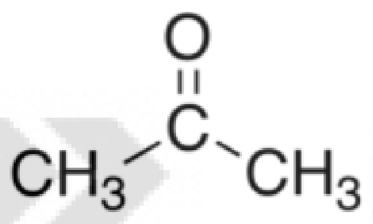
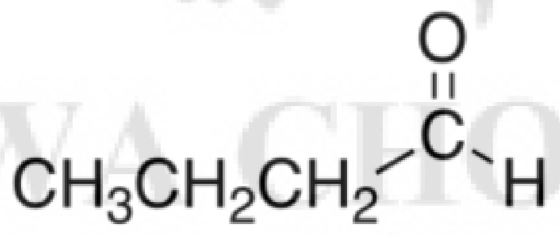
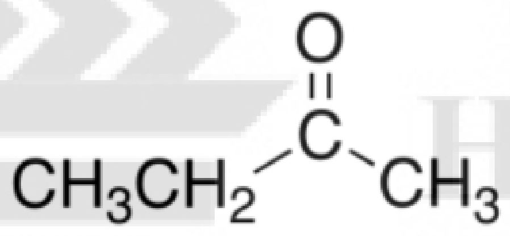
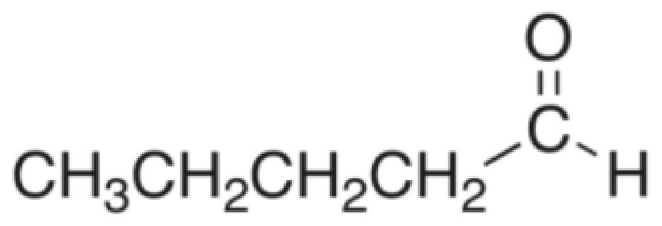
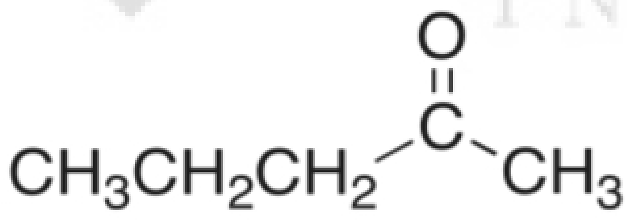
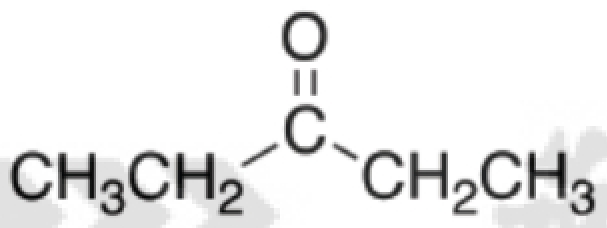
carbonyl functional group

The two simplest types of carbonyl compounds are aldehydes and ketones.

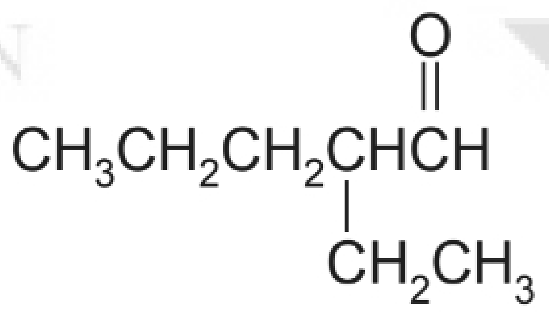
Aldehydes (RCHO)	Ketones (RCOR')
	
R = H, alkyl or aryl *For the 1^{st} member of the aldehydes, R = H, which is methanal, HCHO.*	R/ R' = alkyl or aryl *The 1^{st} member of the ketones can only be propanone, CH_3COCH_3.*
Examples:  benzaldehyde (almonds)  vanilin (vanilla)  cinnamaldehyde (cinnamon)	Examples:  testosterone (male hormone)  carvone (spearmint)  hedione  β-damascenone

1.1 Nomenclature

Alkanes	Aldehydes	Ketones
Name ends in **–e** e.g. propan**e**	Name ends in **-al** e.g. propan**al**	Name ends in **–one** e.g. propan**one**

No. of C atoms	Aldehyde		Ketone	
1		methanal	-	-
2		ethanal	-	-
3		propanal		propanone
4		butanal		butanone
5		pentanal		pentan-2-one
				pentan-3-one

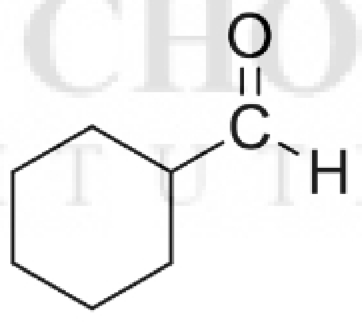
- For aldehydes, the longest chain carrying the –CHO group is considered the parent structure and the –CHO carbon is numbered as carbon 1.



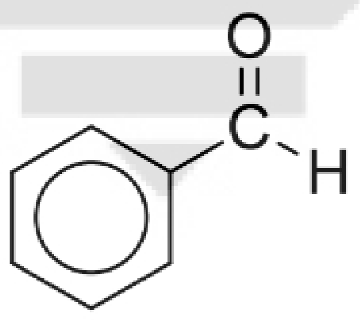
$$CH_3CH_2CH_2\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}H\overset{\displaystyle O}{\overset{\|}{C}}H$$

2-ethylpentanal

- Aldehydes in which the –CHO group is attached directly to a ring system are named by adding the suffix *-carbaldehyde*.



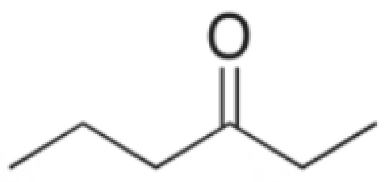
cyclohexanecarbaldehyde



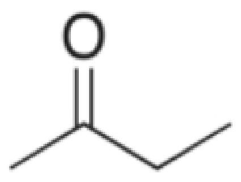
(benzenecarbaldehyde)
benzaldehyde

- For ketones, the parent chain is the longest one that contains the ketone group, and the numbering begins at the end nearer the carbonyl carbon.

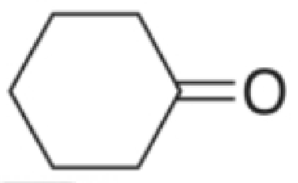
  If the position of the carbonyl group is obvious, the number can be omitted.



hexan-3-one



butanone



cyclohexanone

Lecture Exercise 1.1

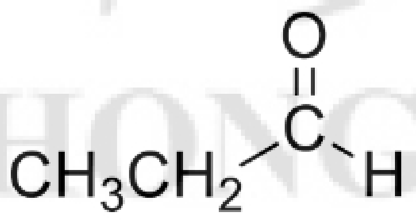
Draw the structural formula of each of the following compounds.

(i) 2-chloro-3-methylbutanal

(ii) 4-phenylpentan-2-one

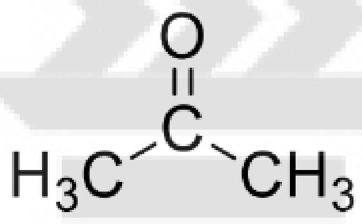
1.2 Isomerism

- Saturated aliphatic aldehydes and ketones have the general formula $C_nH_{2n}O$ where n equals to the number of the carbon atoms in the compound. The aliphatic aldehydes and ketones are constitutional isomers (functional group isomers) if they have the same number of carbon atoms, n, in the compound.



$CH_3CH_2C(=O)H$

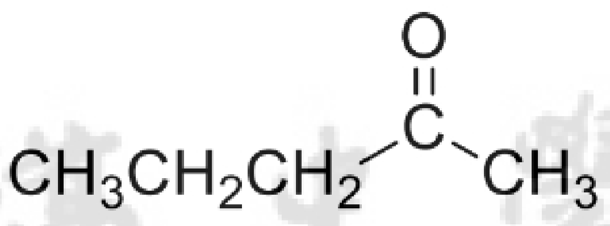
propanal



$H_3C\text{–}C(=O)\text{–}CH_3$

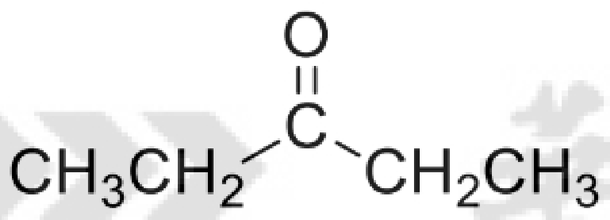
propanone

- For ketones only, the carbonyl group may occur at different positions along the alkyl chain.



$CH_3CH_2CH_2\text{–}C(=O)\text{–}CH_3$

pentan-2-one



$CH_3CH_2\text{–}C(=O)\text{–}CH_2CH_3$

pentan-3-one

2 PHYSICAL PROPERTIES OF ALDEHYDES AND KETONES (Independent Learning subtopic)

2.1 Boiling Points

Aldehydes and ketones have higher boiling points than corresponding non-polar hydrocarbons of similar number of electrons in the molecule, but have lower boiling points than their corresponding alcohols and carboxylic acids.

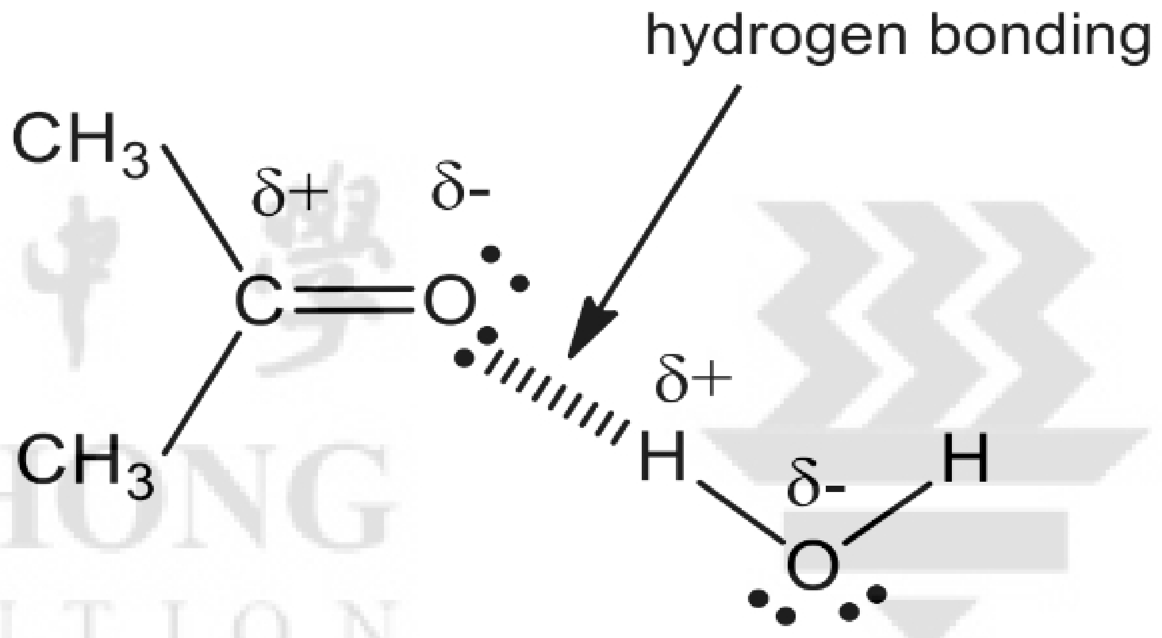
Compound	Structural formula	No. of electrons in the molecule	b.p. / °C	Predominant Intermolecular forces
Butane	$CH_3CH_2CH_2CH_3$	34	–0.5	Dispersion forces
Propanal	CH_3CH_2CHO	32	49	Permanent-dipole - Permanent-dipole
Propanone	CH_3COCH_3	32	56	Permanent-dipole - Permanent-dipole
Propanol	$CH_3CH_2CH_2OH$	34	97	Hydrogen-bonding
Ethanoic acid	CH_3CO_2H	32	118	Hydrogen-bonding

- The **carbonyl** group is **polar**, thus **permanent dipole-permanent dipole** interactions exist between molecules in aldehydes and ketones (in addition to dispersion forces) which require more energy to overcome compared to only dispersion forces present in non-polar alkanes. Hence, carbonyl compounds have **higher** boiling point than the corresponding alkanes.
- **Alcohols** and **carboxylic acids** can form **hydrogen bonds** between molecules, which are **stronger** and require more energy to overcome than **permanent dipole-permanent dipole** interactions in the corresponding aldehydes and ketones. Hence, carbonyl compounds have **lower** boiling point than the corresponding alcohols and acids.

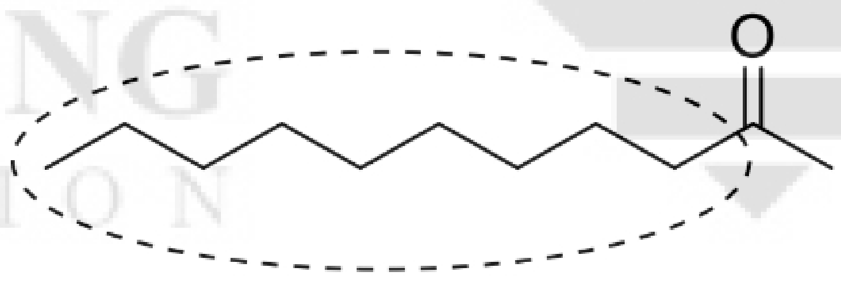
2.2 Solubility in water

Aldehydes and ketones have both polar and non-polar regions. They can act as solvents to both polar and non-polar solutes, which gives them a wide range of uses as solvents.

The lower aliphatic aldehydes and ketones are soluble in water due largely to their ability to form hydrogen bonds with water molecules.



Higher members of carbonyl compounds containing more than 5 carbons or aromatic rings, are virtually insoluble in water. As the number of carbon atoms in the alkyl chain increases, the strength of the dispersion forces between molecules of the carbonyl compound increases. Energy released from hydrogen bonding formed between the carbonyl group and water is less able to overcome the increasingly stronger dispersion forces, as well as the existing hydrogen bonding in water. In addition, the hydrogen bonding with water is disrupted by the larger non–polar alkyl chain.



Non–polar alkyl chain reduces solubility

Self-Practice Question 2.1

The boiling points and solubility in water of some organic compounds are given below:

Compound	Structural formula	No. of electrons in the molecule	b.p. / °C	Solubility in 100g of water/g
A	$CH_3CH_2CH=CH_2$	32	– 6	-
B	$(CH_3)_2CO$	32	56	∞
C	$CH_3CH_2CH_2OH$	34	78	∞
D	CH_3CH_2CHO	32	49	16
E	$CH_3CH_2CH_2CHO$	40	76	7

Explain each of the following.

(a) The boiling point increases in the order, **A** < **B** < **C**.

(b) The solubility of **D** is higher than that of **E**.

3 PREPARATION OF ALDEHYDES AND KETONES

LO 11.6(a): describe the formation of aldehydes and ketones from, and their reduction to, primary and secondary alcohols respectively

Aldehydes can be prepared from:

- Oxidation of primary alcohols (Topic 16 Hydroxy Compounds)

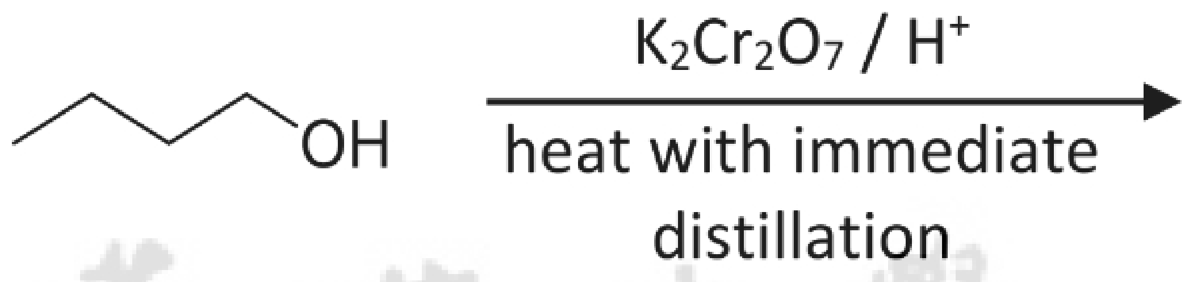
Ketones can be prepared from:

- Oxidation of secondary alcohols (Topic 16 Hydroxy Compounds)
- Oxidative cleavage of substituted alkenes (Topic 11 Alkenes)

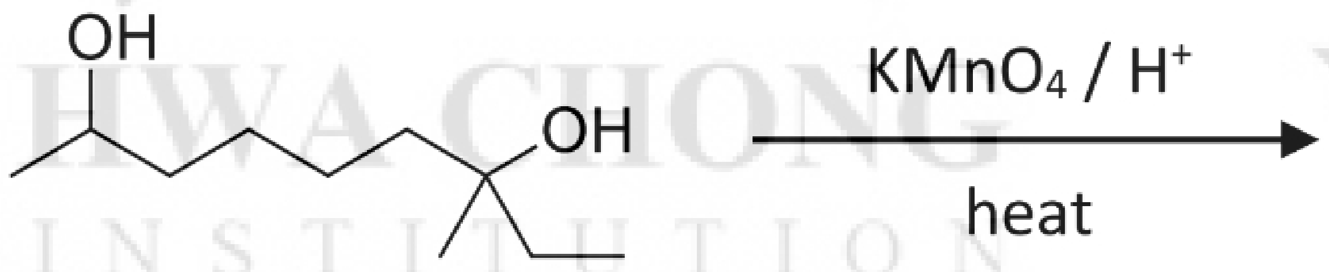
Self-Practice Question 3.1

Draw the products formed from the following reactions:

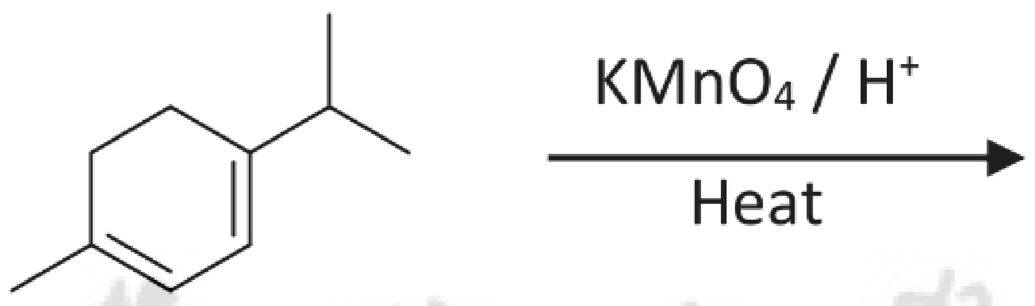
(i)



(ii)



(iii)



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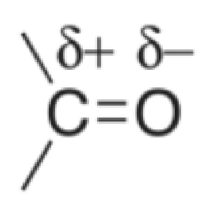
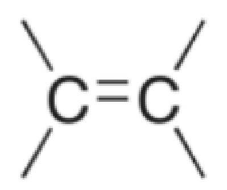
4 REACTIONS OF ALDEHYDES AND KETONES

Reactivity of aldehydes and ketones towards nucleophilic reagents and addition



carbonyl group

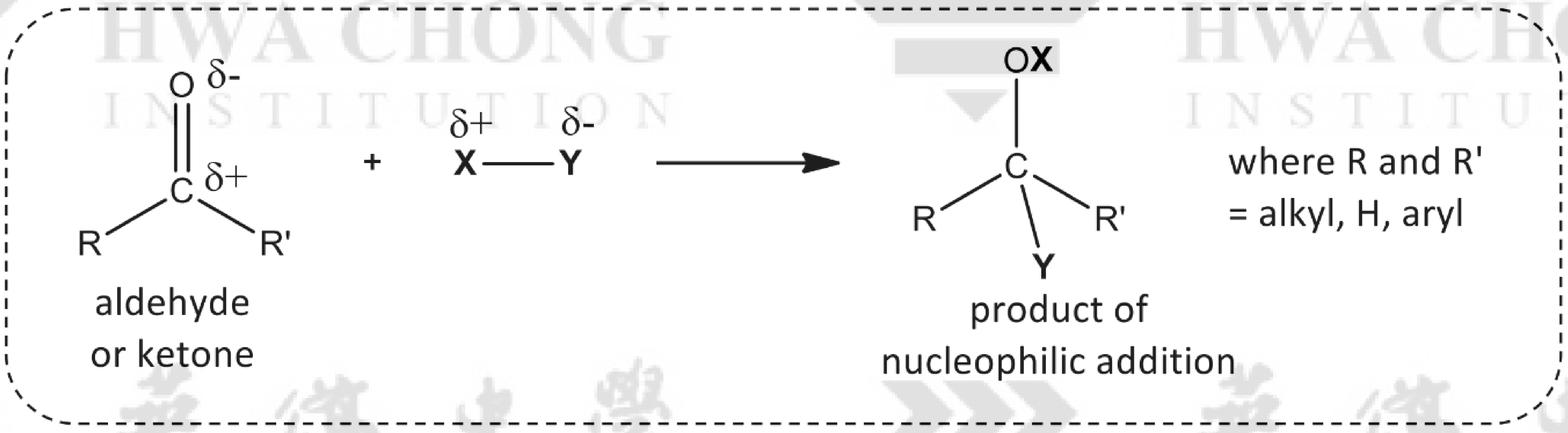


alkene group

- The carbonyl carbon is sp^2 hybridised.
- Carbonyl compounds are therefore planar about the carbonyl carbon and the bond angles are approximately 120° with respect to the carbonyl carbon.
- The unhybridised *p* orbital of carbon overlaps with a *p* orbital of oxygen to form a carbon-oxygen double bond. The carbon-oxygen double bond is made up of one σ and one π bond.
- The C=O bond is similar to the C=C bond and react to saturate the double bond by **addition**.
- However, in the carbonyl functional group, the oxygen atom is much more electronegative than the carbon atom and will attract electron density in the double bond towards itself.
- The carbonyl carbon thus carries a partial positive charge and can be attacked by **nucleophiles**, undergoing nucleophilic addition.
- In contrast, the C=C is non–polar and electron rich, hence it is attacked by **electrophiles** and undergoes electrophilic addition (See Topic 11 Alkenes for electrophilic addition mechanism.)
- Aldehydes and ketones undergo either nucleophilic addition or condensation reactions due to the nucleophilic attack on the carbonyl carbon.

4.1 Nucleophilic Addition Reaction

The overall reaction for nucleophilic addition of carbonyl compounds can be represented as:



Examples of nucleophiles that can react with aldehydes and ketones in a nucleophilic addition include CN^-, H_2O and ROH.

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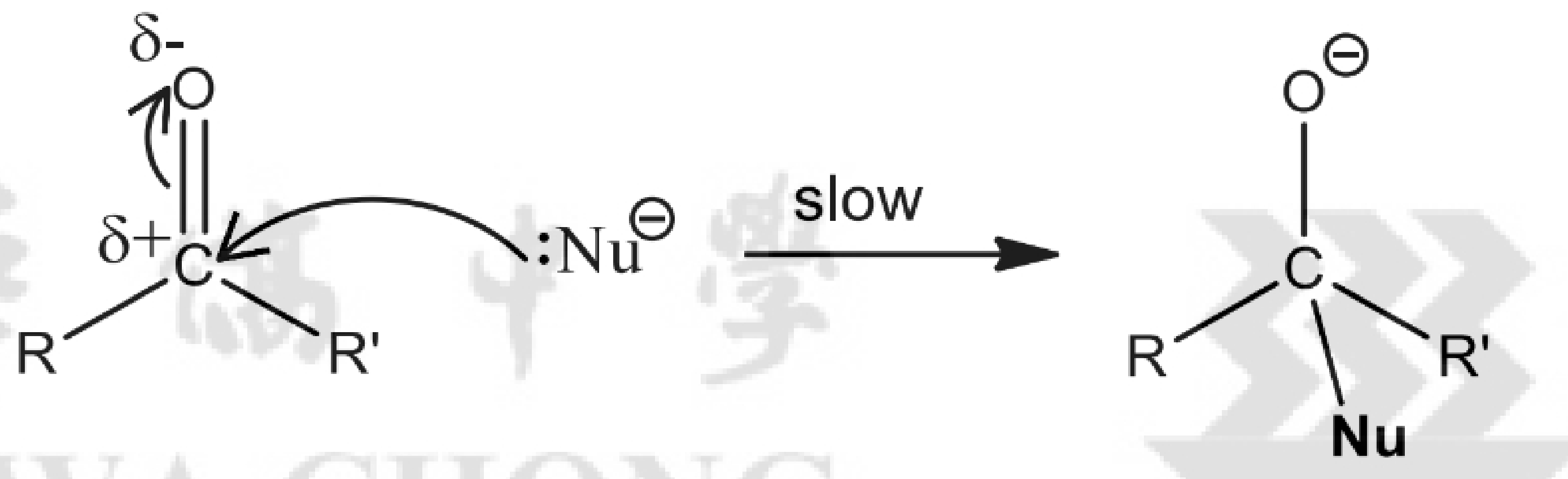
4.1.1 General mechanism of nucleophilic addition

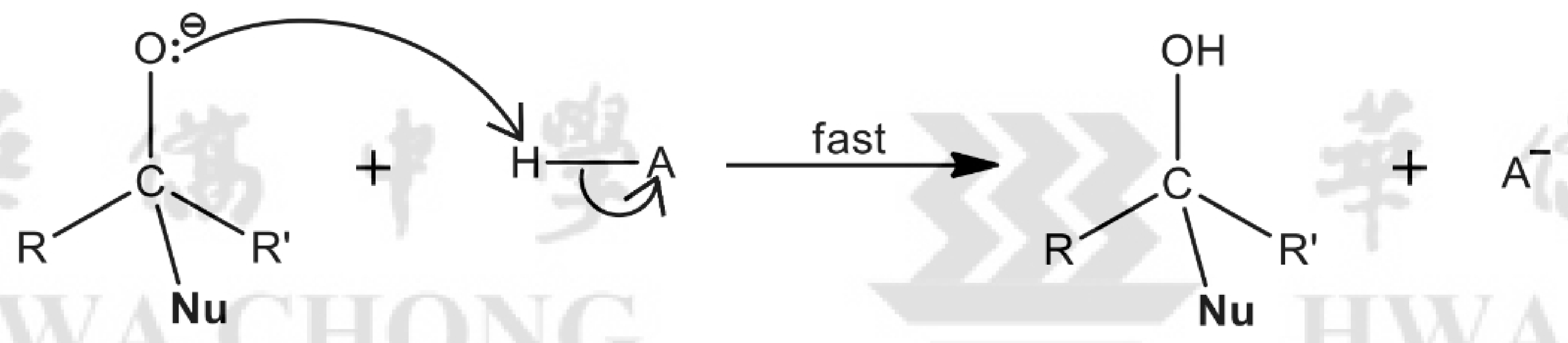
Step 1: A nucleophile attacks the electron-deficient carbonyl carbon, breaking the π bond of the C=O group, to form an alkoxide ion.



where R and R' = alkyl, H, aryl

tetrahedral intermediate

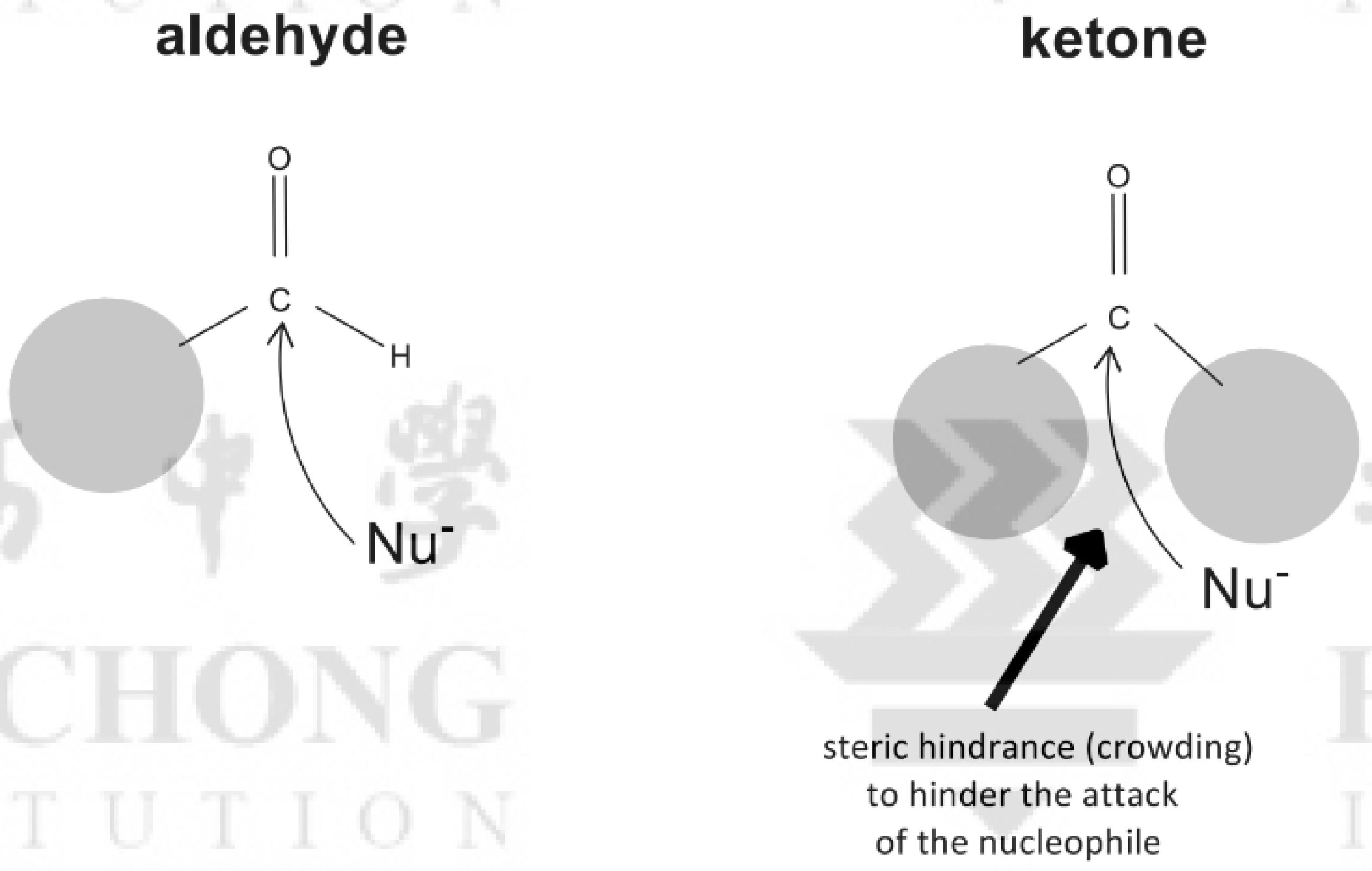
Step 2: The tetrahedral intermediate is protonated by water or acid to give an alcohol as the final product.



4.1.2 Relative Reactivity of Aldehydes and Ketones in Nucleophilic Addition Reactions

Aldehydes are generally more reactive than ketones in nucleophilic addition reactions for both steric and electronic reasons.

(i) Steric reason:
The presence of two relatively large substituents in ketones versus only one large substituent in aldehydes means that attacking nucleophiles are able to approach the carbonyl carbon in aldehydes with less steric hinderance than in ketones.



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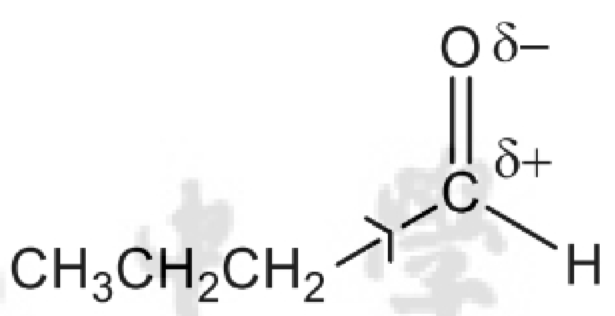
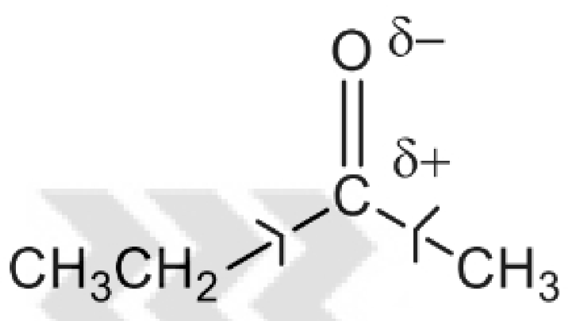
(ii) Electronic reason:

Aldehydes have one electron donating alkyl group while ketones have two. Hence, the carbonyl carbon of aldehydes has a higher partial positive charge compared to that of ketones, making it more susceptible towards nucleophilic attack.



aldehyde

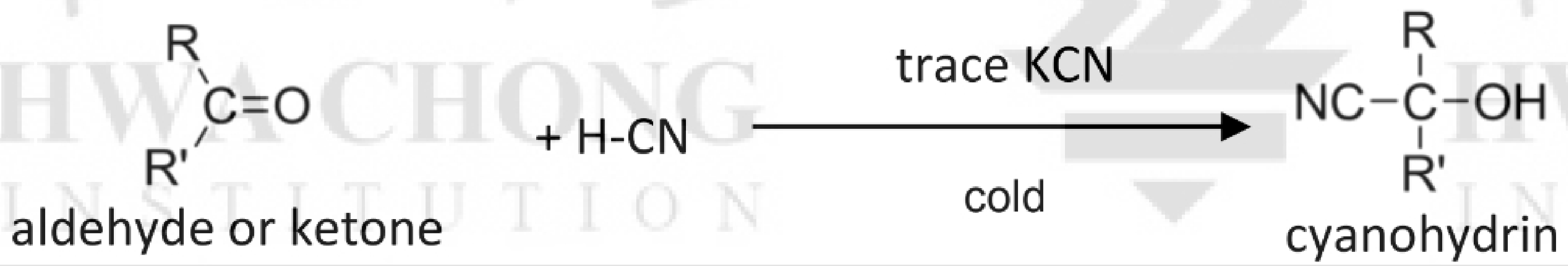


ketone

4.1.3 Nucleophilic addition with hydrogen cyanide, HCN

LO 11.6(b): describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones

Aldehydes and ketones undergo nucleophilic addition reaction with hydrogen cyanide, HCN, under appropriate conditions to form cyanohydrins.



Reagents and conditions:	HCN with trace KCN, cold
Comments:	KCN is used as a catalyst; CN^- ion is regenerated at the end of the reaction.

Note:

HCN is a toxic gas and has a boiling point of 25.6°C . It is usually generated *in situ* by the reaction between KCN(s) and cold dilute H_2SO_4.

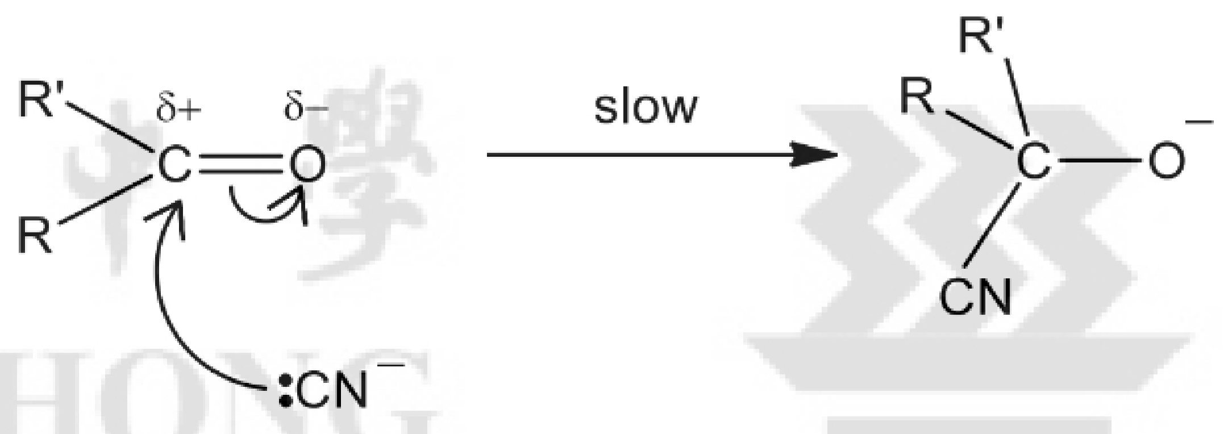
$$2\ KCN + H_2SO_4 \rightarrow K_2SO_4 + 2\ HCN$$

The reaction mixture is kept cold (at 10-20°C) to ensure that HCN remains as a liquid under reaction conditions.

Mechanism

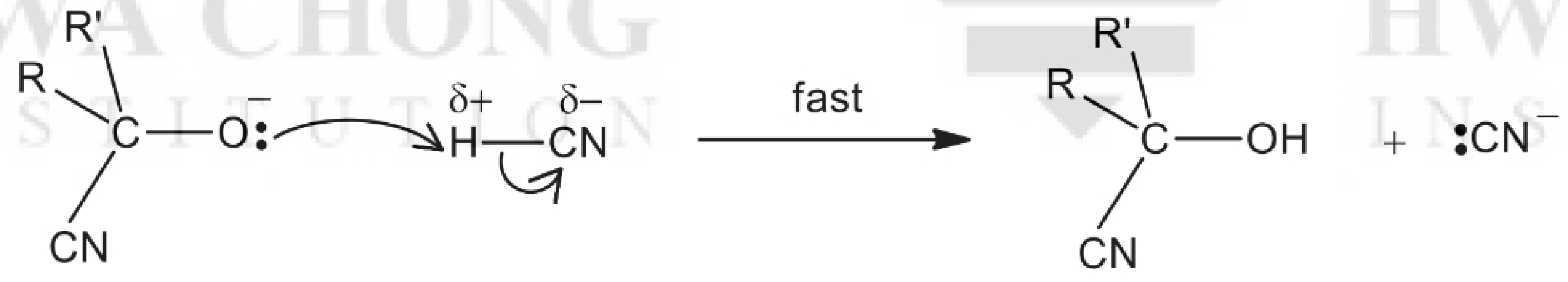
The mechanism of the nucleophilic addition with HCN involves two steps:

Step 1: The carbonyl carbon is attacked by the CN^- nucleophile

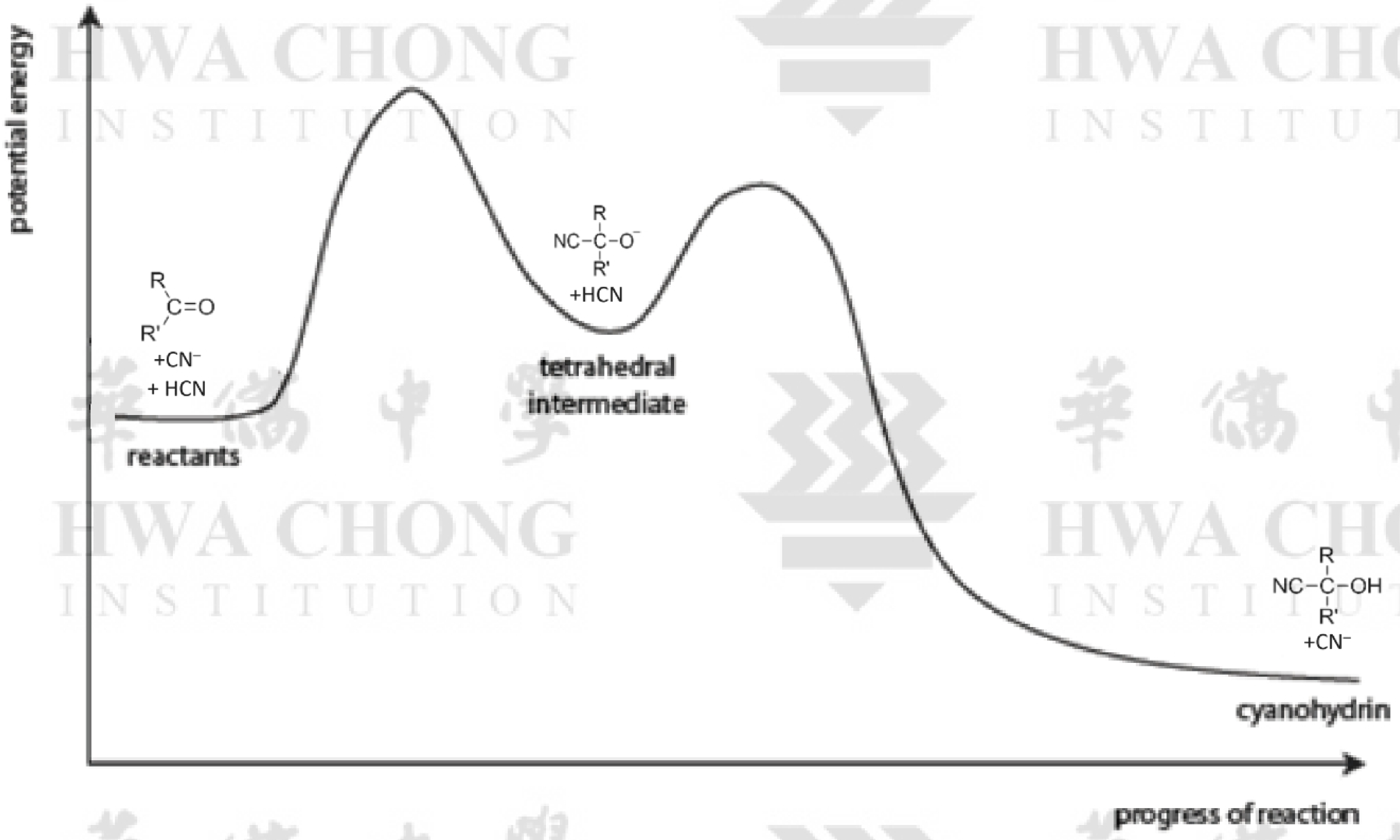


- The CN^- ion acts as nucleophile and attacks the electron-deficient carbonyl carbon breaking the π-bond of the C=O.
- This leads to the formation of a stable tetrahedral intermediate anion (an alkoxide ion).
- This is the rate-determining step.

Step 2: Protonation of the intermediate to give a cyanohydrin



- The tetrahedral alkoxide ion intermediate is protonated by attacking an undissociated polar HCN molecule to yield the cyanohydrin.
- The CN^- nucleophile is regenerated.



Kinetics

This nucleophilic addition mechanism is ***bimolecular***, as it involves both the carbonyl compound and the nucleophile **:**CN^- in the ***rate-determining*** step. Hence, the rate equation is:

$$\text{rate} = k\,[\text{carbonyl compound}]\,[CN^-]$$

To increase the rate of reaction, the following methods are used:

1. add a trace amount of KCN as catalyst

- HCN is a weak acid, which only partially ionises in water to give CN^-.

$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^- \qquad K_a = 6.2 \times 10^{-10}\ \text{mol dm}^{-3}$$

- The reaction takes place very slowly if only HCN is used because the solution contains a very low concentration of CN^- ions.
- The reaction can be speeded up by adding a trace amount of KCN, a salt which completely dissociates to provide free CN^- ions.

$$KCN\,(aq) \rightarrow K^+(aq) + CN^-(aq)$$

- CN^- ions used in the addition reaction are regenerated at the end of the reaction as shown in the mechanism.

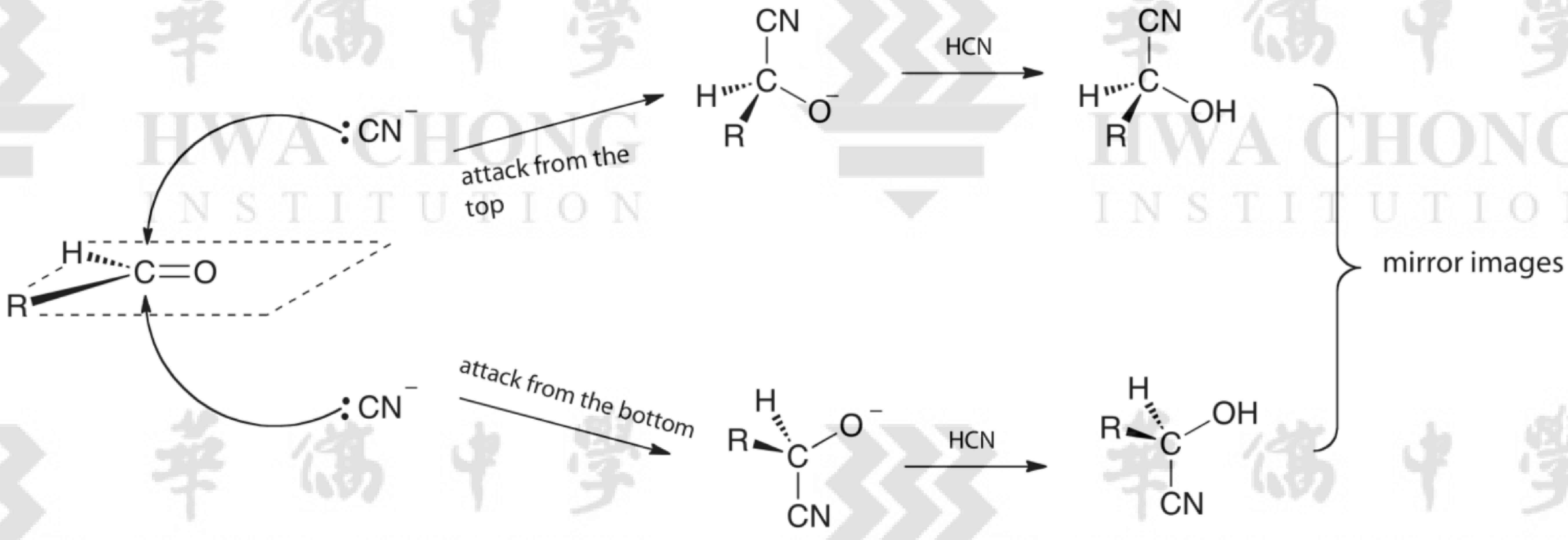
2. add a small amount of base (e.g. NaOH)

$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$$

When a small amount of base is added, the H_3O^+ ions are neutralised, which by Le Chatelier's Principle, shifts the position of the above equilibrium to the right such that the concentration of the CN^- increases. Hence the rate of reaction increases.

Stereochemistry

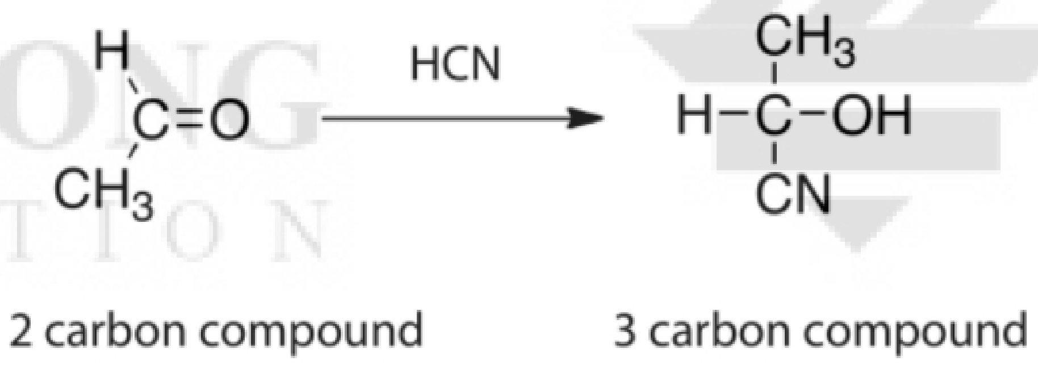
The geometry about the carbonyl carbon atom in aldehydes and ketones is planar. Hence the nucleophile can attack the δ+ carbonyl carbon atom in equal probability from the top or bottom of the plane, producing equal amounts of both enantiomers to give a racemic mixture, if the resulting sp^3 carbon is chiral.



Refer to the similar circumstances leading to the formation of racemic mixtures in Topic 11 Alkenes and Topic 13 Halogen Derivatives. In electrophilic addition and S_N1 mechanisms, the **geometry about** the *positively-charged carbon in the carbocation intermediate* is also **planar**, allowing a nucleophile to attack from either side of the plane with equal probability.

Importance of cyanohydrins in synthesis

- Nucleophilic addition with CN^- ion is an important method of lengthening the carbon chain by 1 carbon (step-up reaction).

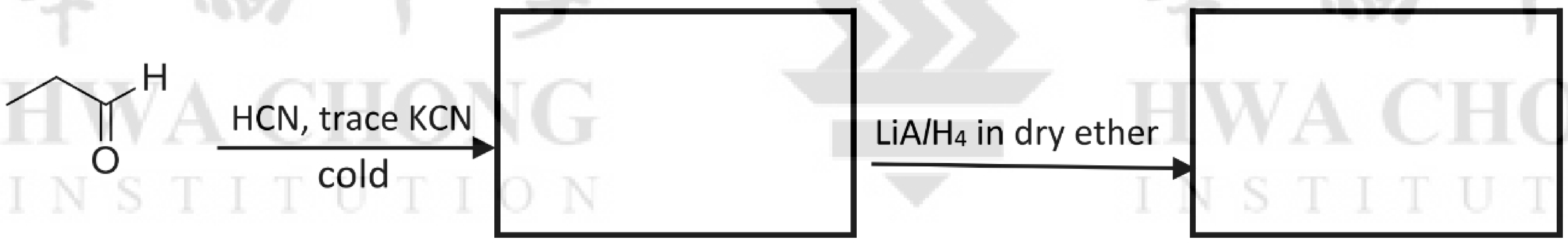


- The cyanohydrin product can be easily converted to other usable forms since the nitrile group (–CN) can be converted to other functional groups such as:
  - carboxylic acids by acid hydrolysis using mineral acids such as dilute H_2SO_4
  - carboxylate salts by alkaline hydrolysis using alkalis such as dilute NaOH
  - amines by reduction using lithium aluminium hydride (LiA/H_4) in dry ether or hydrogen with nickel catalyst

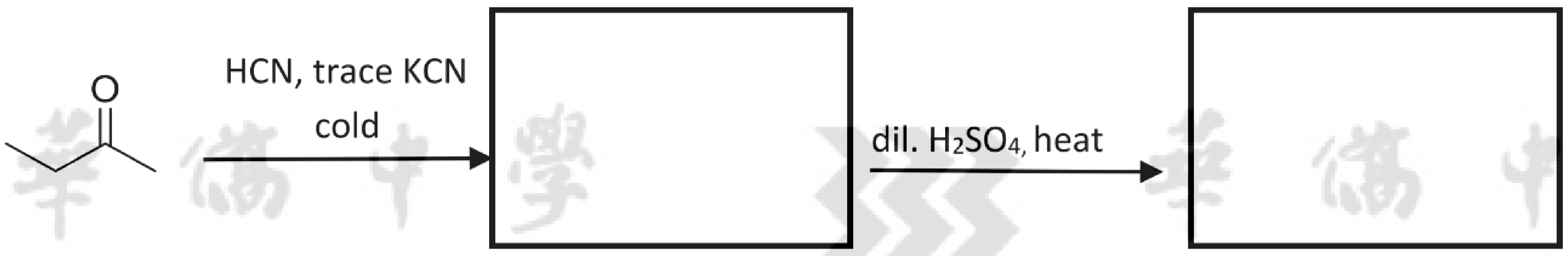
Lecture Exercise 4.1

Draw the products formed from the following reactions:

(i)



(ii)



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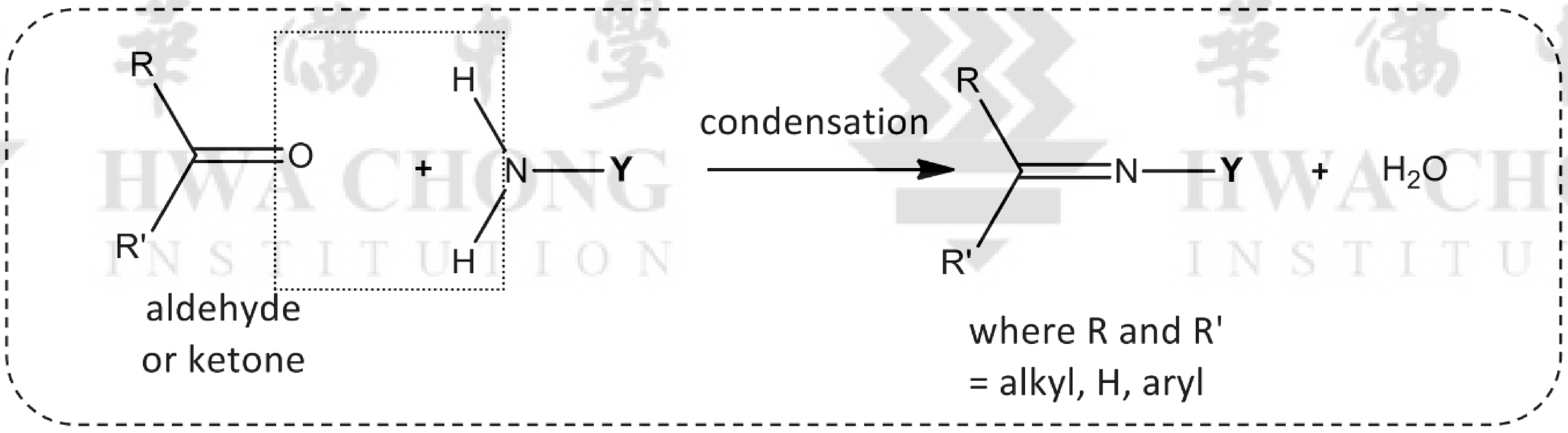
4.2 Condensation Reaction (Application Example)

Nucleophiles having two H atoms on a nitrogen atom readily add on to carbonyl compounds. But usually, the initially formed addition product is not isolated because it easily loses water via elimination to give stable compounds containing a C=N bond.

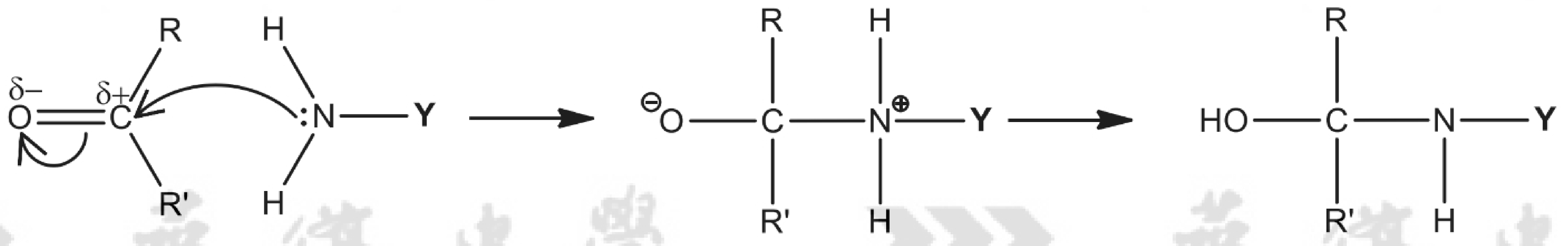
The overall reaction can be represented as:



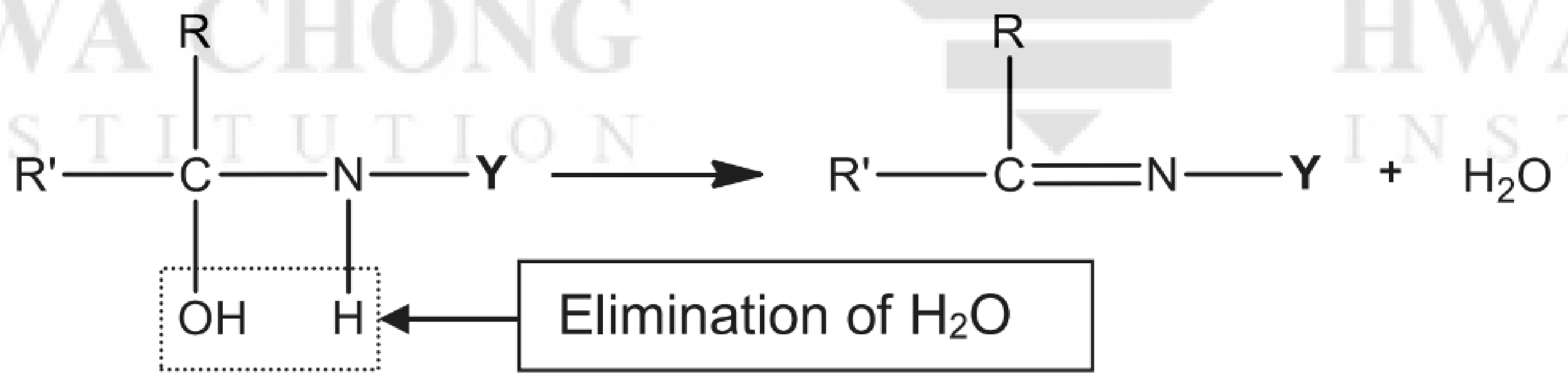
4.2.1 General Mechanism

The reaction can be viewed as an addition, followed by an elimination, hence it may be referred to as an *addition-elimination* reaction.

Step 1: Addition of nucleophile to carbonyl compound



Step 2: Elimination of a water molecule

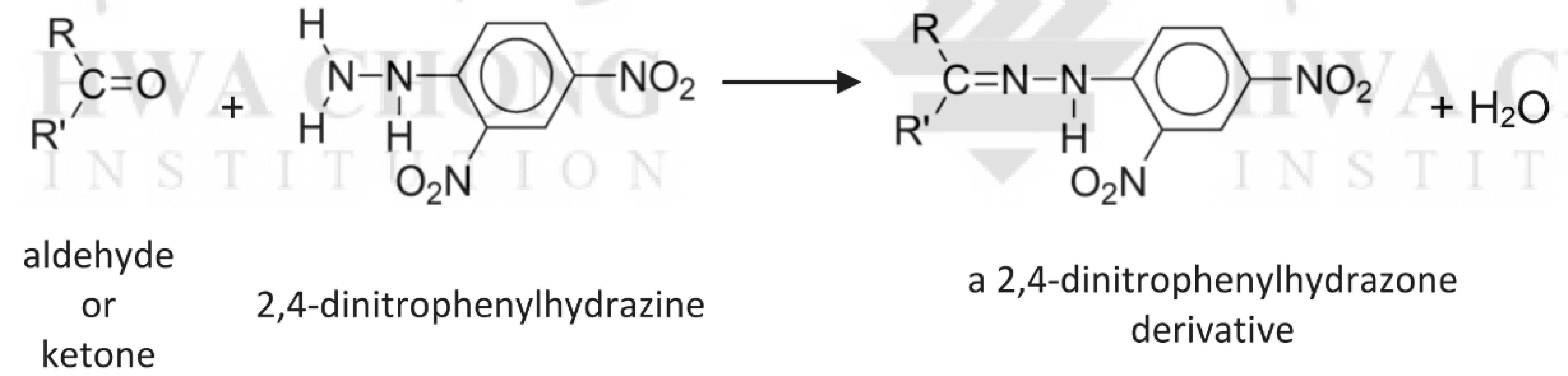


4.2.2 Condensation reaction with 2,4-dinitrophenylhydrazine (2,4-DNPH)

LO 11.6(d): describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) to detect the presence of carbonyl compounds

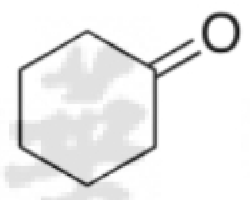
2,4-dinitrophenylhydrazine, also known as Brady's reagent, is a yellow solution. It reacts with aldehydes and ketones to form 2,4-dinitrophenylhydrazone, which is an orange precipitate. A water molecule is eliminated in the reaction.

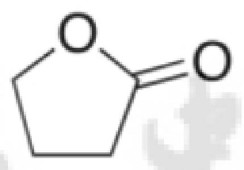
This is a characteristic test for the presence of aldehydes and ketones.



Reagents and conditions:	2,4-dinitrophenylhydrazine (2,4-DNPH), room temperature
Observations:	Orange precipitate formed

Lecture Exercise 4.2
Which of the following compounds will give an orange precipitate with 2,4-dinitrophenylhydrazine?


A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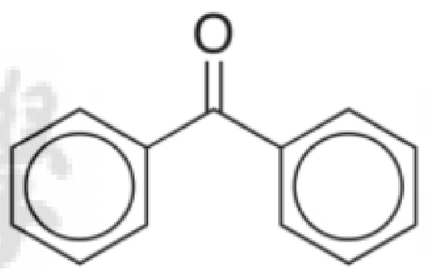
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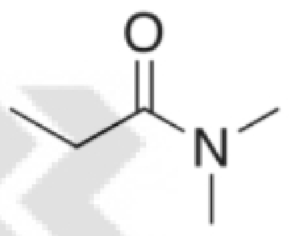
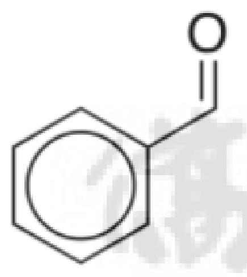
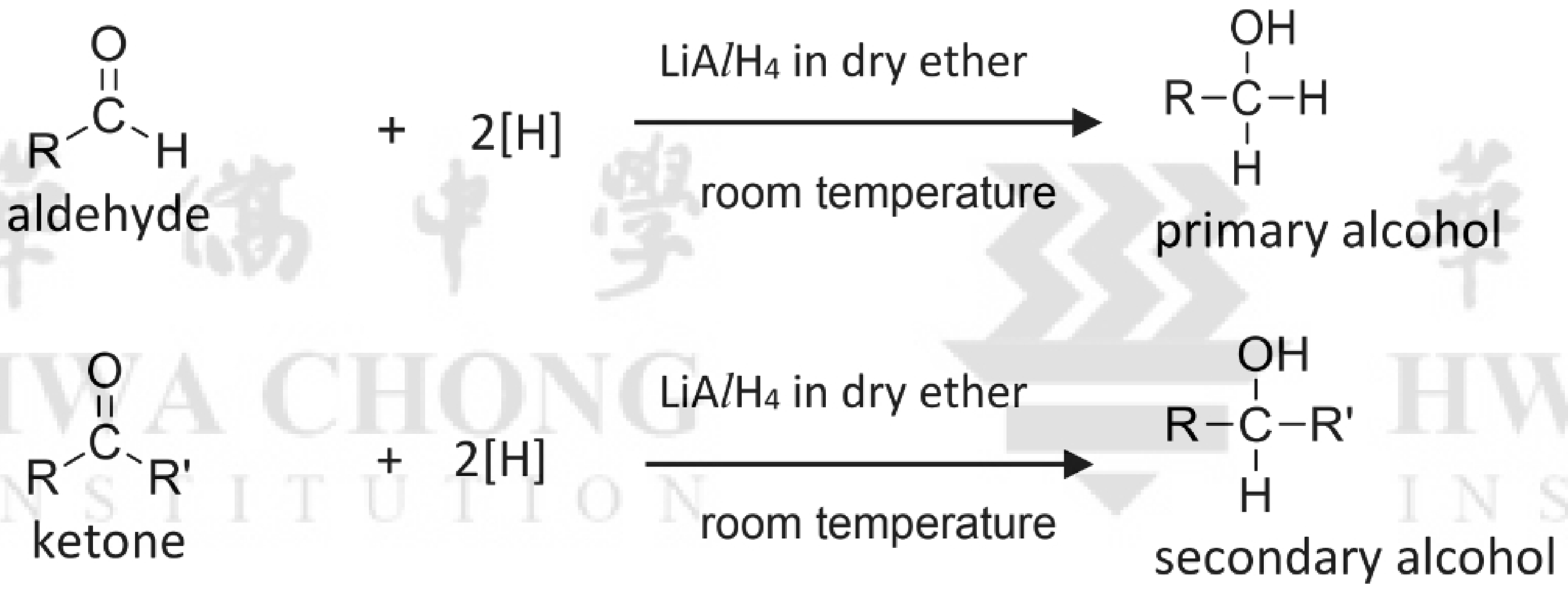

D


E

4.3 Reduction

Aldehydes and ketones undergo reduction to form primary and secondary alcohols respectively.



Reagents and conditions:	$LiAlH_4$ in dry ether, room temperature **Note:** When the aldehyde or ketone react with $LiAlH_4$, the alkoxide ion is form. H_2O needs to be added to protonate the alkoxide to form the alcohols.
Comments:	Other reducing agents like $NaBH_4$ in methanol or, $H_2(g)$/ Ni at high pressure may be used.

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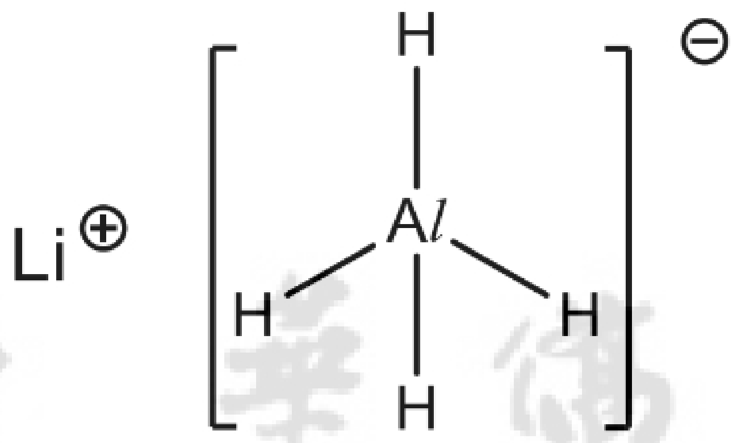
4.3.1 Comparing reducing agents $LiAlH_4$ and $NaBH_4$

LO 11.6(c)part: explain the differences in reactivity between carbonyl compounds and alkenes towards nucleophilic reagents, such as lithium aluminium hydride



Lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$) are useful hydride reagents that can reduce aldehydes and ketones in excellent yields.

- $LiAlH_4$ is a grayish powder that is soluble in ether. It reacts violently with water to form H_2 gas and decomposes explosively when heated above 120 °C. $NaBH_4$ is a white, crystalline solid that can be handled in the open atmosphere and used in either water or alcohol solution.

- Due to the hazardous nature of $LiAlH_4$ and ether (which forms highly explosive mixtures in air), the use of $NaBH_4$ is usually preferred.

- Both $LiAlH_4$ and $NaBH_4$ can be considered as sources of the nucleophilic hydride anion, H^-. They both have hydrogen atoms covalently bonded to aluminium and boron respectively and because hydrogen is more electronegative than aluminium and boron, the hydrogen atoms will bear the negative charge, making it a good nucleophile. As such, $LiAlH_4$ and $NaBH_4$ are able to react with aldehydes and ketones bearing the polar C=O group with an electron-deficient carbon.

- Aluminium is less electronegative than boron, thus more of the negative charge in the AlH_4^- ion is borne by the hydrogen atoms. Therefore, $LiAlH_4$ is a much stronger reducing agent, and is much less selective than $NaBH_4$.

- Both $LiAlH_4$ and $NaBH_4$ do not reduce the non-polar electron-rich alkene group. The alkene functional group is reduced using $H_2(g)$ over a nickel catalyst. Refer to Topic 6 Reaction Kinetics for the mechanism of this heterogeneous catalysis reaction.

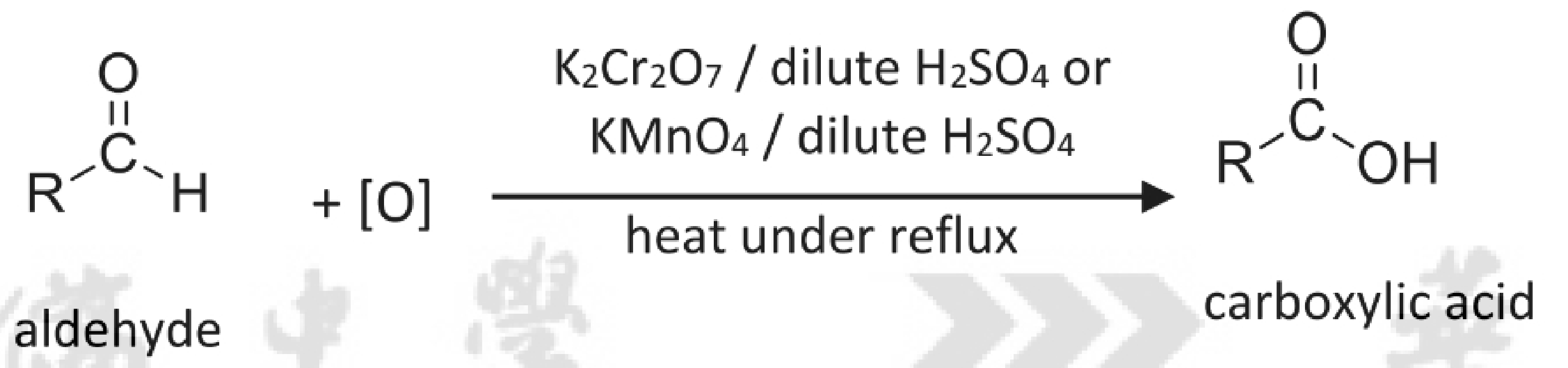
4.4 Oxidation

LO 11.6(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)

The aldehyde functional group undergoes oxidation reactions with acidified potassium dichromate (VI), Tollens' reagent and Fehling's solution, while the ketone does not. As such, these three tests are good distinguishing tests between aldehydes and ketones.

4.4.1 Oxidation with acidified potassium dichromate(VI) or acidified potassium manganate(VII)

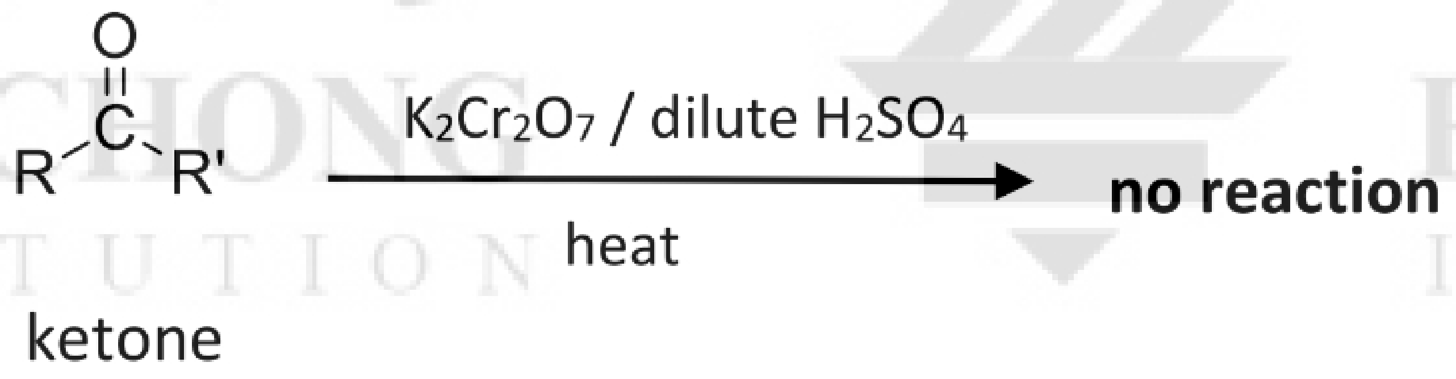
Aldehyde has a hydrogen atom attached directly to the carbonyl carbon. This enables it to be oxidised to carboxylic acids.



Reagents and conditions: $K_2Cr_2O_7$ / dilute H_2SO_4 or $KMnO_4$ / dilute H_2SO_4, heat under reflux

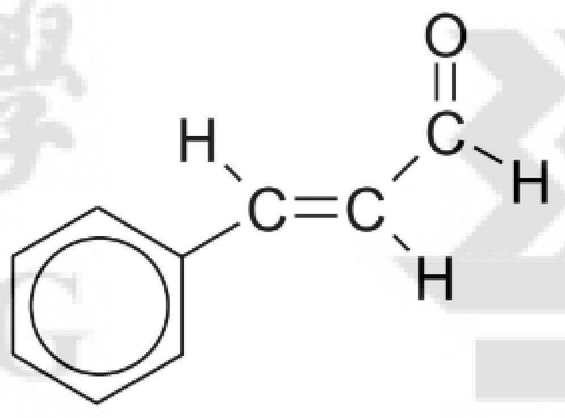
Comments: Orange solution ($Cr_2O_7^{2-}$) turns green (Cr^{3+}) or
Purple solution (MnO_4^-) turns colourless (Mn^{2+})

Ketones do not have a hydrogen atom attached directly to the carbonyl carbon, thus are not easily oxidised.



Lecture Exercise 4.3

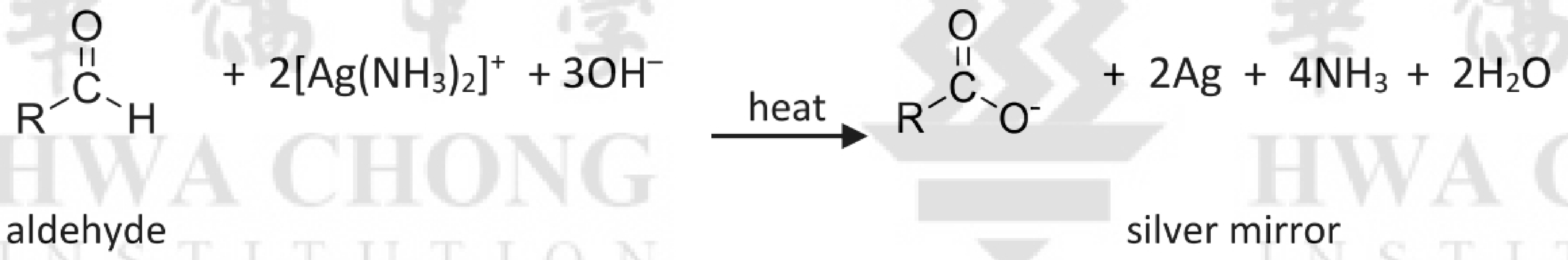
How would you oxidise only the aldehyde functional group in cinamaldehyde to carboxylic acid?



4.4.2 With Tollens' reagent (Silver Mirror Test)

Tollens' reagent (ammoniacal silver nitrate) contains diamminesilver(I) ions, $[Ag(NH_3)_2]^+$.

Aldehydes reduce silver(I) in Tollens' reagent to silver metal. Under carefully controlled conditions, silver metal will deposit on the walls of the reaction vessel as a mirror.



$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \xrightarrow{\text{heat}} RCOO^- + 2Ag + 4NH_3 + 2H_2O$$

Reagents and conditions: Tollens' reagent, heat

Observations: Silver mirror formed

Comments: $[Ag(NH_3)_2]^+$ is unstable and should always be freshly prepared. It can be prepared as follows:

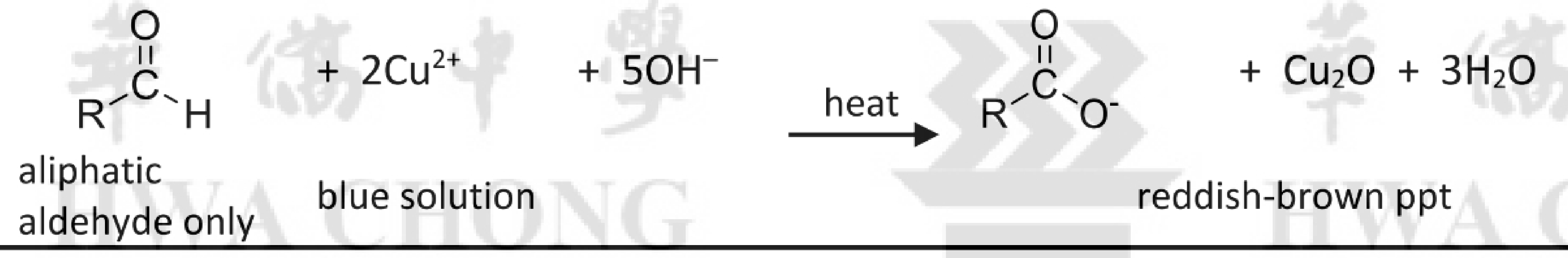
1. One drop of dilute NaOH(aq) is added to about 3 cm^3 of $AgNO_3$(aq) to produce a dark brown precipitate of Ag_2O.

2. Dilute NH_3(aq) is then added dropwise until the brown precipitate first formed just redissolves.

4.4.3 With Fehling's reagent

Fehling's reagent is an alkaline solution of copper(II) tartrate.

Aldehydes (except benzaldehyde and its derivatives) reduce the copper(II) in Fehling's reagent to the reddish-brown copper(I) oxide, which is precipitated.

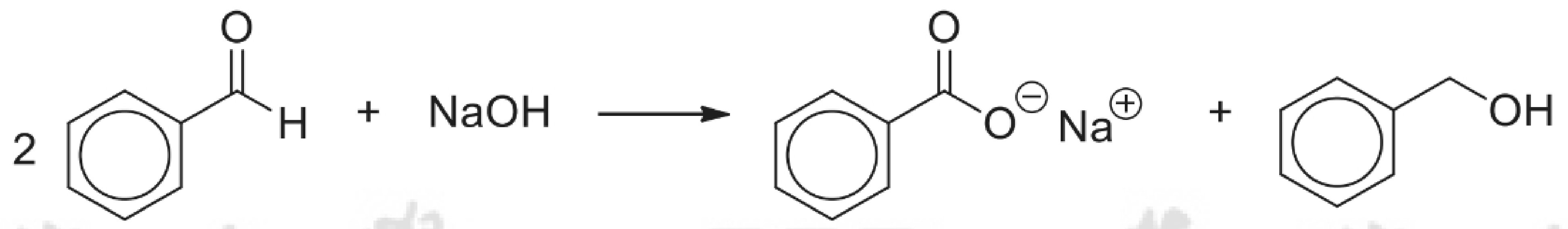


Reagents and conditions: Fehling's reagent, heat

Observations: Reddish-brown (brick-red) precipitate formed

Comments: Ketones, benzaldehyde and its derivatives do not reduce Fehling's reagent.

In fact, benzaldehyde undergoes disproportionation instead due to the presence of NaOH in Fehling's reagent.

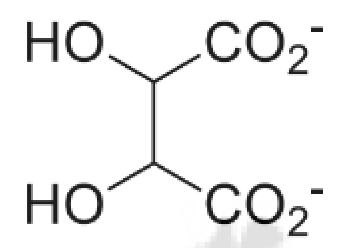


Fehling's reagent deteriorates on keeping. and is usually prepared in two parts which are added together just before the test is carried out.

It consists of:

1. Fehling's solution A ($CuSO_4$ solution) and
2. Fehling's solution B (sodium potassium tartrate + excess NaOH)

A deep blue solution is obtained on mixing the two solutions owing to the formation of copper(II) tartrate, the tartrate ions present prevent the precipitation of $Cu(OH)_2$ by complexing with the copper(II) ions.



tartrate ion

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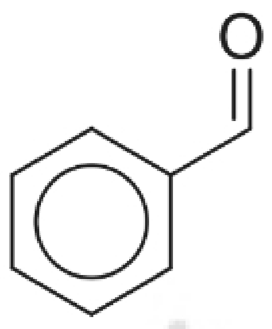
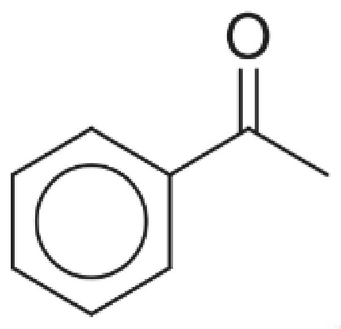
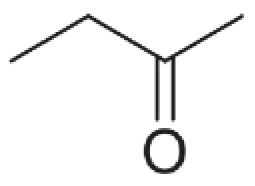
Lecture Exercise 4.4

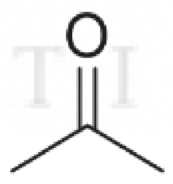
(i) Which of the following compounds will give a positive Tollens' reagent test?

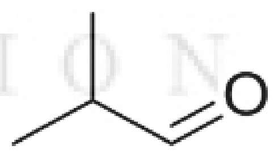

X


Y


Z

(ii) Which of the following compounds will reduce Fehling's reagent?


A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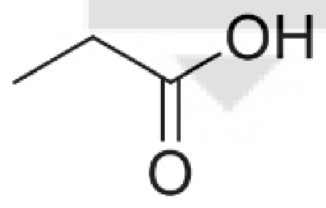
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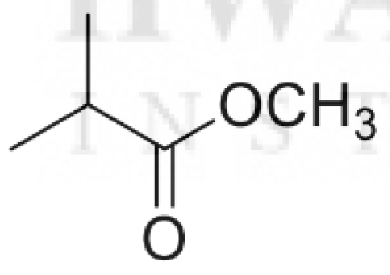
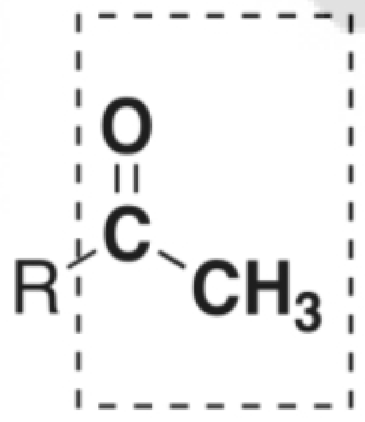

D

4.5 Tri-iodomethane (iodoform) Test

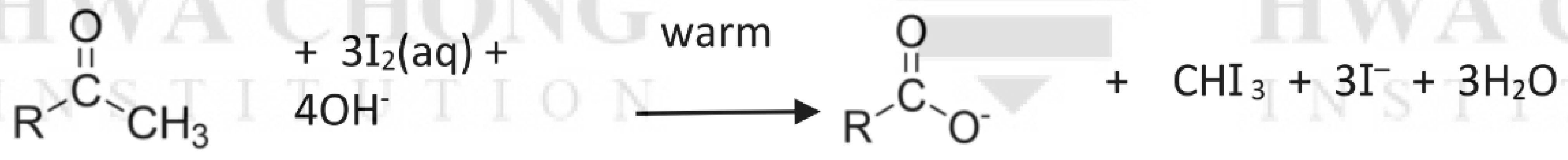
LO 11.6(f):deduce the presence of a $CH_3CO^–$ group from its reaction with alkaline aqueous iodine to give tri-iodomethane

This test specifically identifies aldehydes and ketones with the structure:



"R" can be a hydrogen atom or a hydrocarbon group (alkyl or aryl).

If "R" is hydrogen, the compound is ethanal, CH_3CHO. Ethanal is the only aldehyde that gives positive tri-iodomethane test.



ethanal or methyl ketones

carboxylate ion

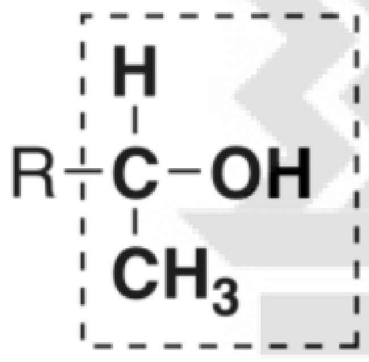
iodoform

Reagents and conditions:	Aqueous I_2 with NaOH(aq), warm
Observations:	Yellow crystals of CHI_3 (iodoform) formed.

Note:

This reaction breaks a C–C bond and removes a methyl (-CH_3) group. It is therefore a useful method of shortening a carbon chain by a single carbon atom (step-down reaction).

Recall: Alcohols with the structure below also give a positive tri-iodomethane test. Refer to the triiodomethane test in Topic 16 Hydroxy Compounds.



Lecture Exercise 4.5

Suggest a structure for each of the isomers, **X**, **Y** and **Z** of the compound $C_3H_6O_2$, based on the following reactions:

X: gives tri-iodomethane with aqueous alkaline iodine and reduces Fehling's solution;

Y: gives tri-iodomethane with aqueous alkaline iodine but does not reduce Fehling's solution;

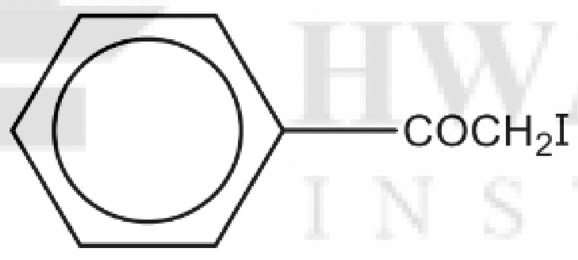
Z: does not give tri-iodomethane with aqueous alkaline iodine but does reduce Fehling's solution.

Lecture Exercise 4.6

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 $Cl_3CO_2CH_3$

[N2010/1]

Summary of Distinguishing Tests

Reagents & Conditions	Aldehyde	Benzaldehyde	Ketone	Comments
2,4-DNPH	+	+	+	• A characteristic test for aldehydes and ketones • All other functional groups will give negative results. • This test differentiates aldehydes and ketones from ALL other functional groups.
$K_2Cr_2O_7$ / dilute H_2SO_4 Heat	+	+	–	• Good test to differentiate aldehydes and benzaldehydes from ketones.
Tollens' reagent, Heat	+	+	–	• Another method to differentiate aldehydes from ketones. • ALL aldehydes give positive Tollens' Test.
Fehling's reagent, Heat	+	–	–	• Good test to further differentiate aldehydes from benzaldehydes.

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Self-Practice Question 4.1

Describe a simple chemical test to differentiate the following sets of compounds:

(i) butanal and butanone

(ii) propanone and propan-1-ol

(iii) propanal, propanone and benzaldehyde

Summary of reactions of aldehydes and ketones

State the reagents and conditions needed for the conversions on the arrows below: