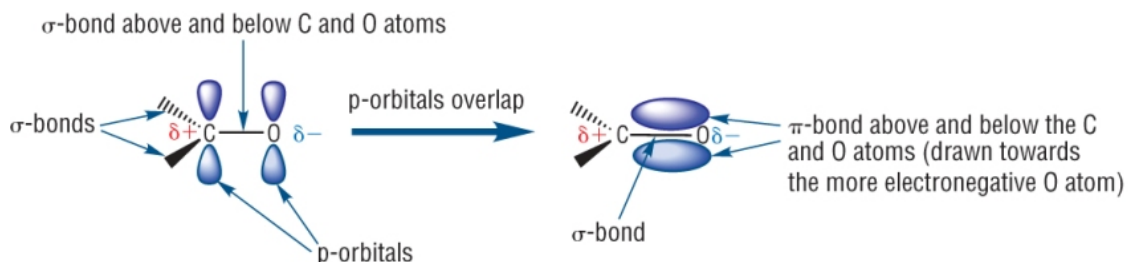


## 3.8 Aldehydes and ketones

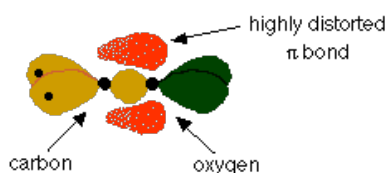
### Introduction:

#### p's to $\pi$ 's

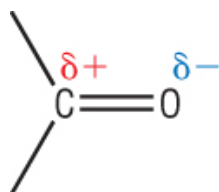
- Like the alkenes, the carbonyl group consists of a  $\sigma$  bond and a  $\pi$  bond between the carbon and oxygen:



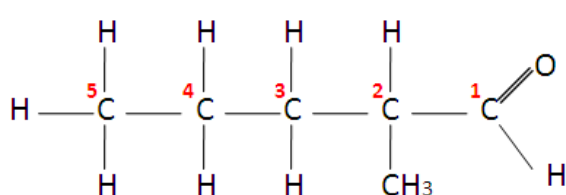
- Oxygen is more electronegative than carbon meaning that the  $\pi$  electrons will be highly distorted towards the oxygen atom as shown above.



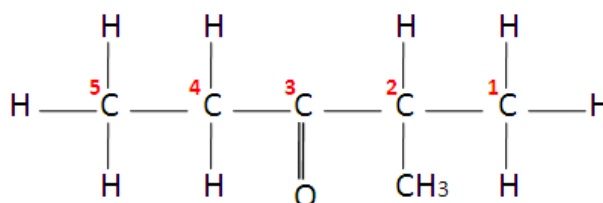
- This sets up a permanent dipole across the C=O bond:



### Naming aldehydes and ketones:



**2-Methylpentanal**

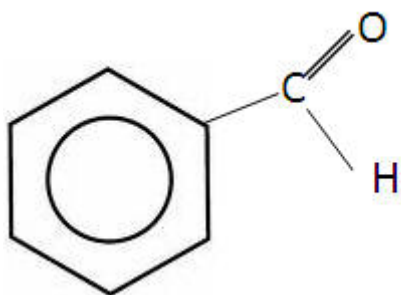


**2-methylpentan-3-one**

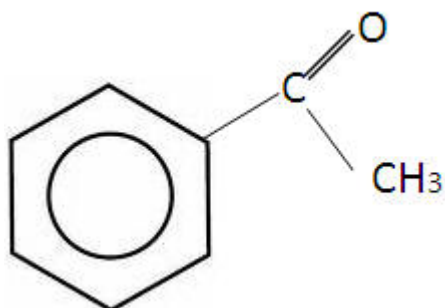
- In aldehydes, the aldehyde carbon always starts at 1.
- In ketones, the ketone (or carbonyl group) is always counted to give it the smallest possible number.

## Aromatic aldehydes and ketones:

- The simplest aldehyde is benzaldehyde and the simplest ketone is phenylethanone:



**Benzaldehyde**



**Phenylethanone**

- These aromatic aldehydes and ketones have a fragrant smell, often found naturally in foods.

## Naming aldehydes and ketones

- Give the IUPAC name of the following:

Structure	IUPAC name
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$	
$\text{CH}_3\text{COCH}_2\text{CH}_3$	
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{COCH}_3$	

- Draw the structure of the following:

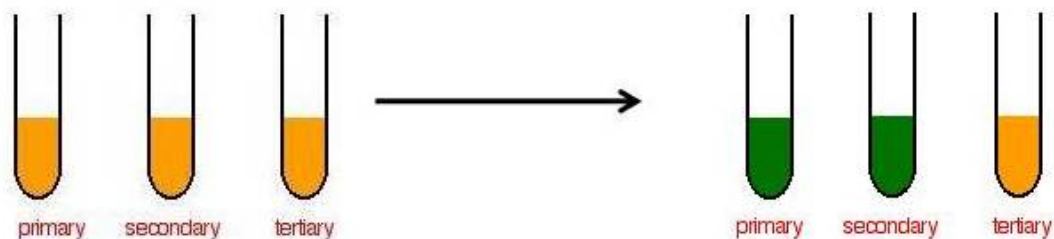
<b>Alcohol</b>	<b>Structural formula</b>	<b>Skeletal formula</b>
Propanone		
Pentanal		
Hexan – 3 – one		

- Complete the table below for pentanal

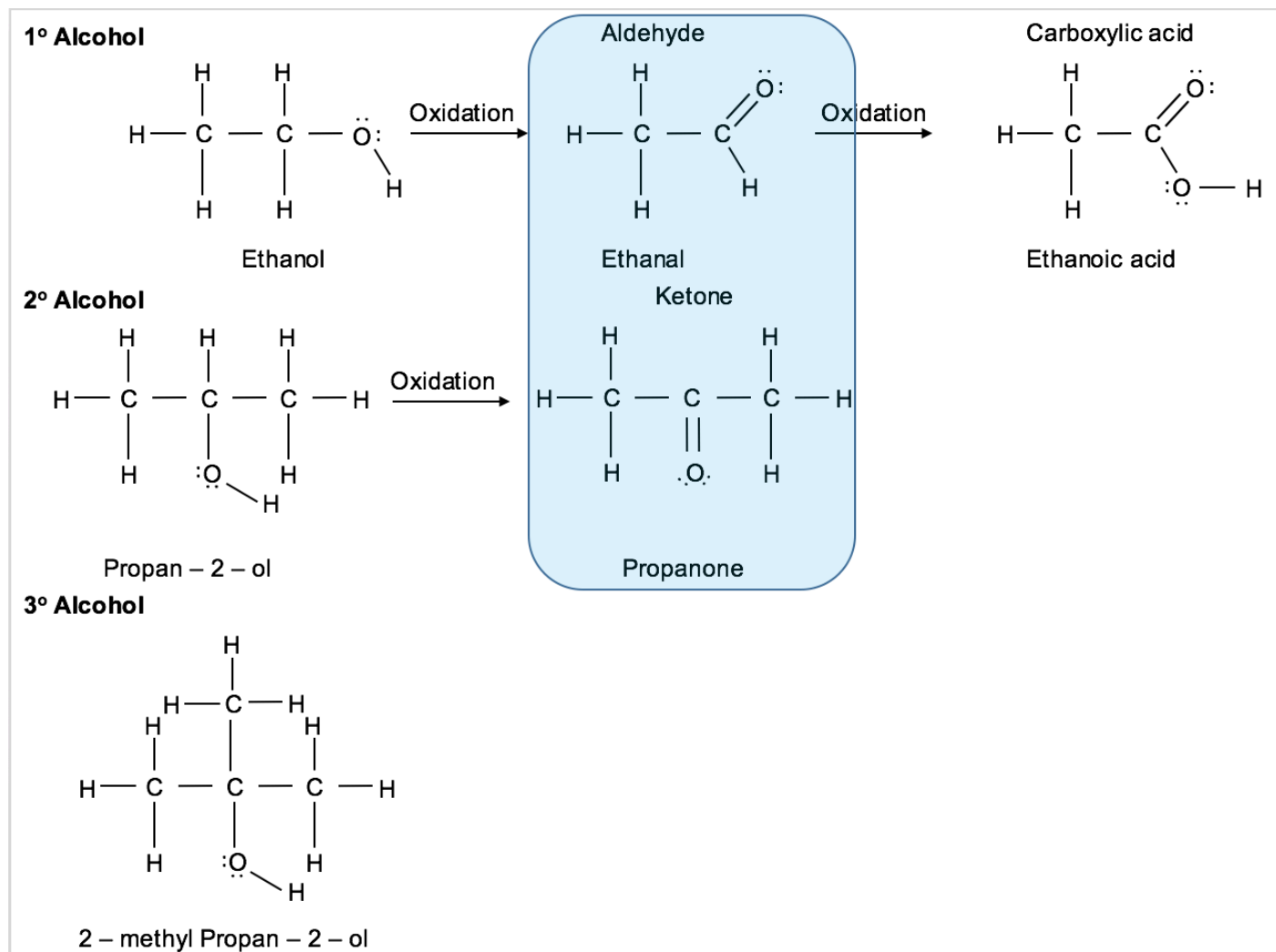
<b>Structural formula</b>	<b>Functional group Isomer</b>	<b>Chain Isomer</b>

## A recap – Oxidation forming aldehydes and ketones:

- Aldehydes and ketones are made by the oxidation of 1° and 2° alcohols.



- $K_2Cr_2O_7 / H_2SO_4$  is the oxidising agent which changes colour from orange to green



## Test for aldehydes and ketones

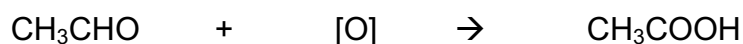
### 1) Tollens' reagent – Silver mirror test

Reagents                      **Silver nitrate dissolved in ammonia,  $\text{Ag}(\text{NH}_3)_2^+$**

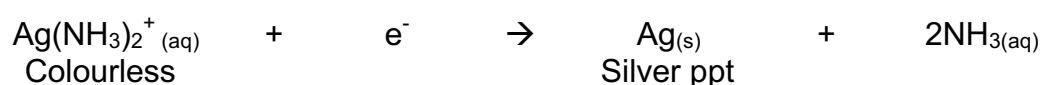
Observations                **Aldehyde      Silver precipitate / mirror formed**  
   **Ketone        No reaction**

Chemical reactions

Organic: Aldehyde is oxidised to a carboxylic acid



Reagent: Silver ions are reduced to silver



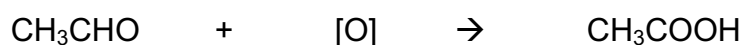
### 2) Fehling's solution –

Reagents                       **$\text{CuSO}_4$  /  $\text{NaOH}$  / Warm**

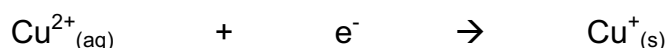
Observations                **Aldehyde      Red precipitate**  
   **Ketone        No reaction**

Chemical reactions

Organic: Aldehyde is oxidised to a carboxylic acid



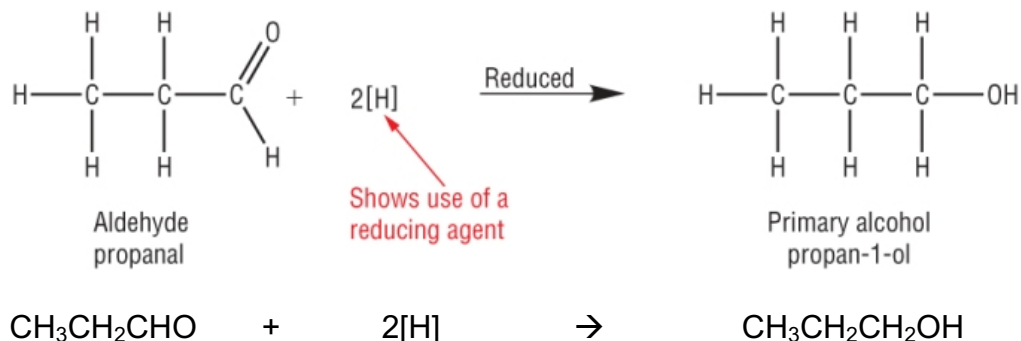
Reagent:  $\text{Cu}^{2+}$  ions are reduced to  $\text{Cu}^+$



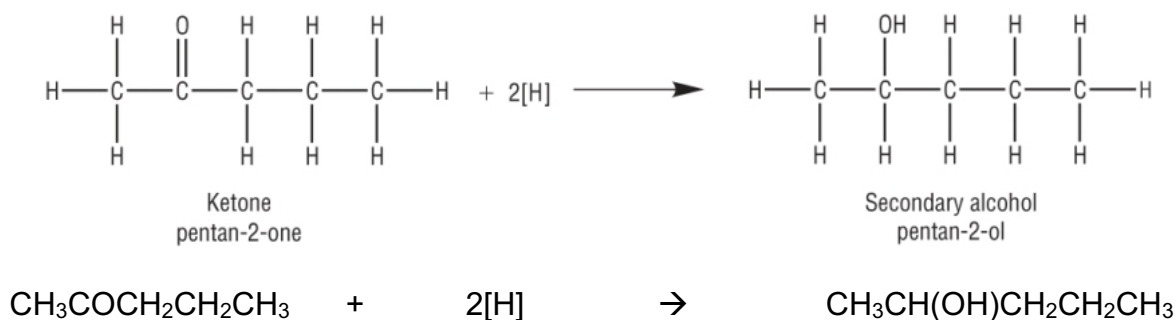
## Reducing aldehydes and ketones

- Aldehydes and ketones can be reduced back to the primary or secondary alcohol.
- Reducing agent used is sodium tetrahydridoborate (III), NaBH<sub>4</sub>.
- The reaction(s) are complex so we use [H] in the equation.

### Reduction of aldehydes:

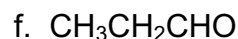
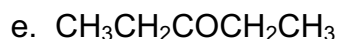
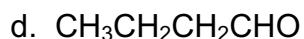
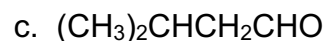
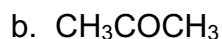
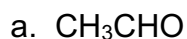


### Reduction of ketones:

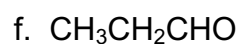
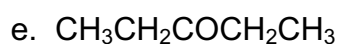
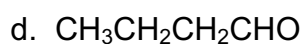
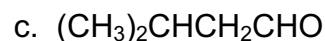
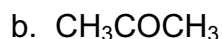
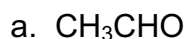


### Questions:

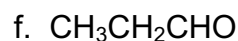
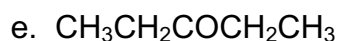
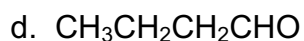
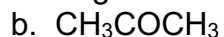
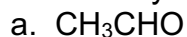
1) Name the following molecules:



2) Draw, classify and name the alcohols made from the reduction of the following

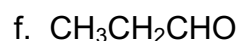
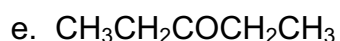
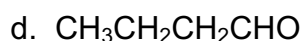
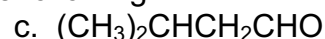
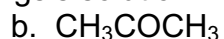
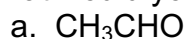


3) What would you observe if Tollen's reagent was added to the following?



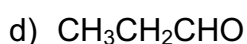
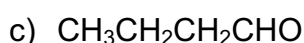
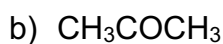
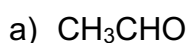
g. Explain your observations using chemical equations and state what has been oxidised and reduced. Use one of the molecules that gives a positive result in your answer:

4) What would you observe if Fehlings's solution was added to the following?



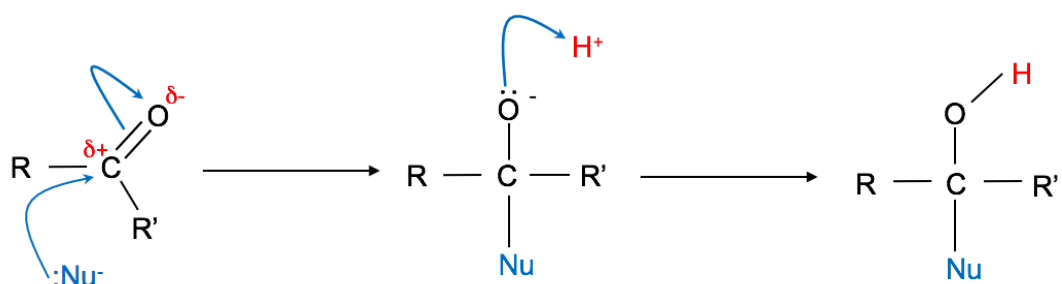
g. Explain your observations using chemical equations and state what has been oxidised and reduced. Use one of the molecules that gives a positive result in your answer:

5) Reduction of aldehydes and ketones to alcohols are carried out using  $\text{NaBH}_4$ . Write balanced chemical equations for the following. Use  $[\text{H}]$  as the reducing agent.



## Nucleophilic addition reactions:

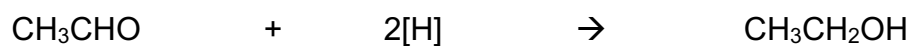
### General:



Aldehyde / Ketone

- The nucleophile is attracted to the  $\delta^+$  carbon in the carbonyl group.

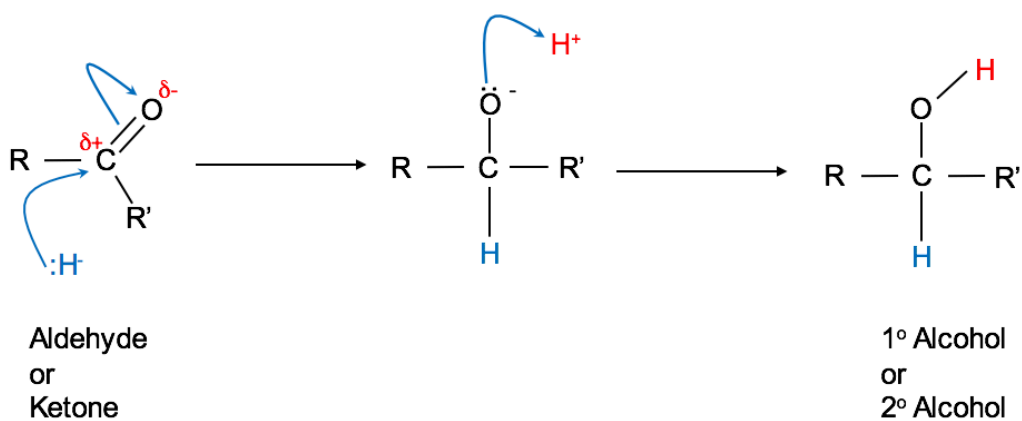
### 1) Reduction



**Conditions:**  $\text{NaBH}_4$  - a source of hydride ions,  $\text{H}^-$

- This is the nucleophile and is attracted to the  $\delta^+$  carbon in the carbonyl group.

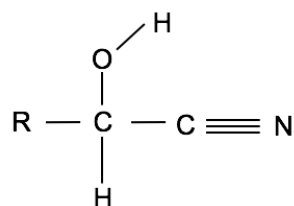
### The Mechanism:



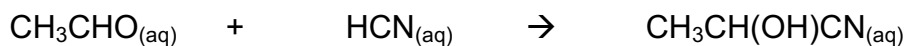


## 2) Hydroxynitriles

General formula:



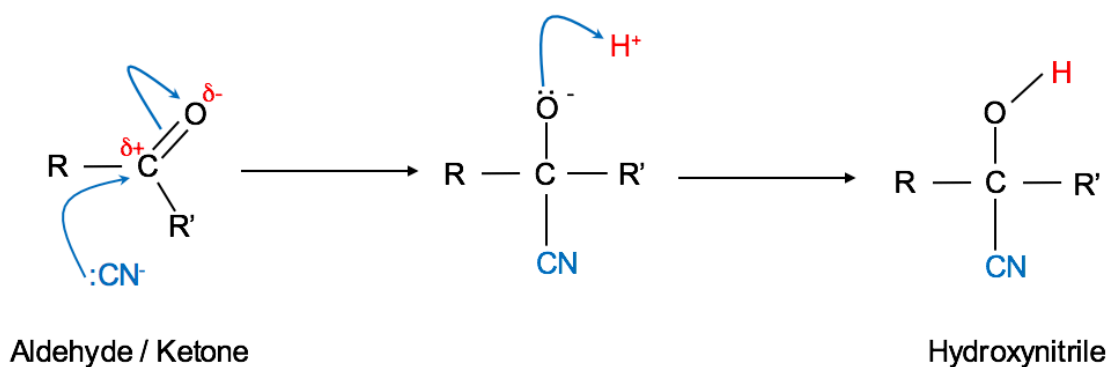
Formation:



**Conditions:** KCN followed by dilute acid (HCl) – This produces HCN

- $\text{CN}^-$  is the nucleophile and is attracted to the  $\delta^+$  carbon in the carbonyl group.

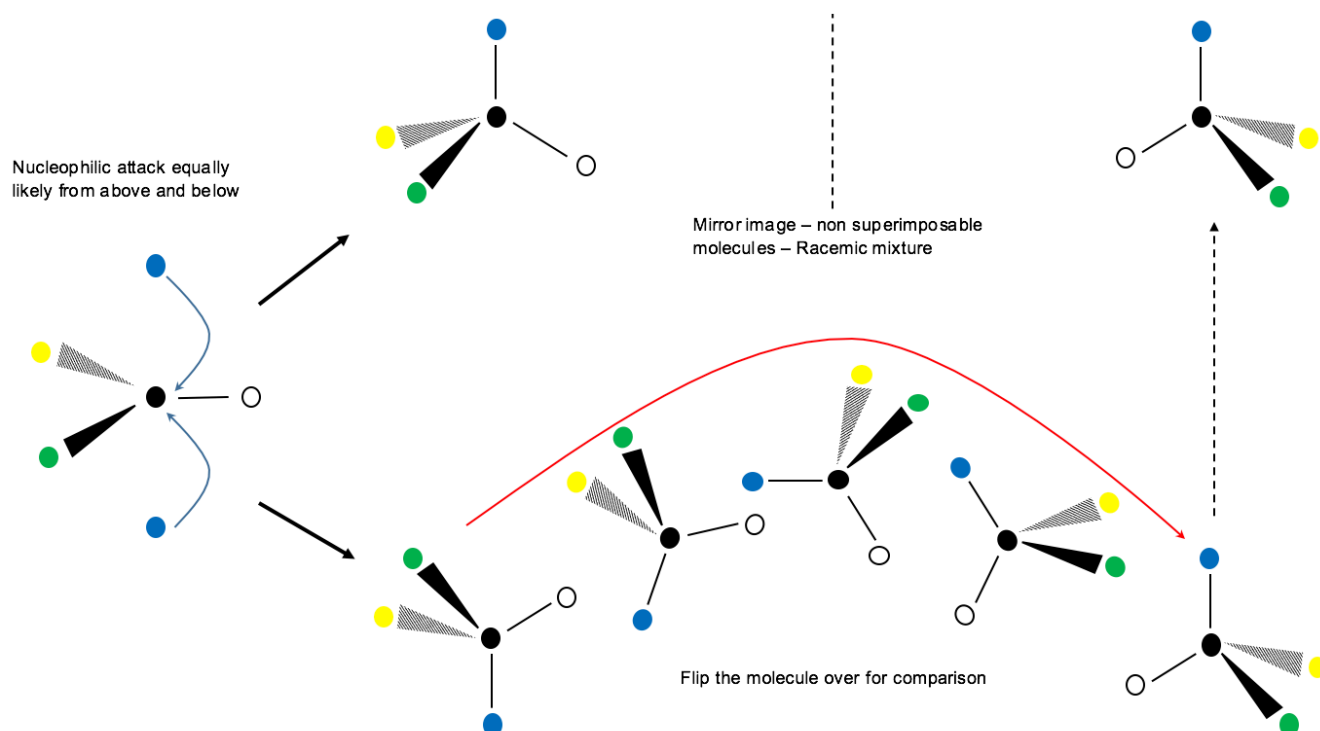
The Mechanism:



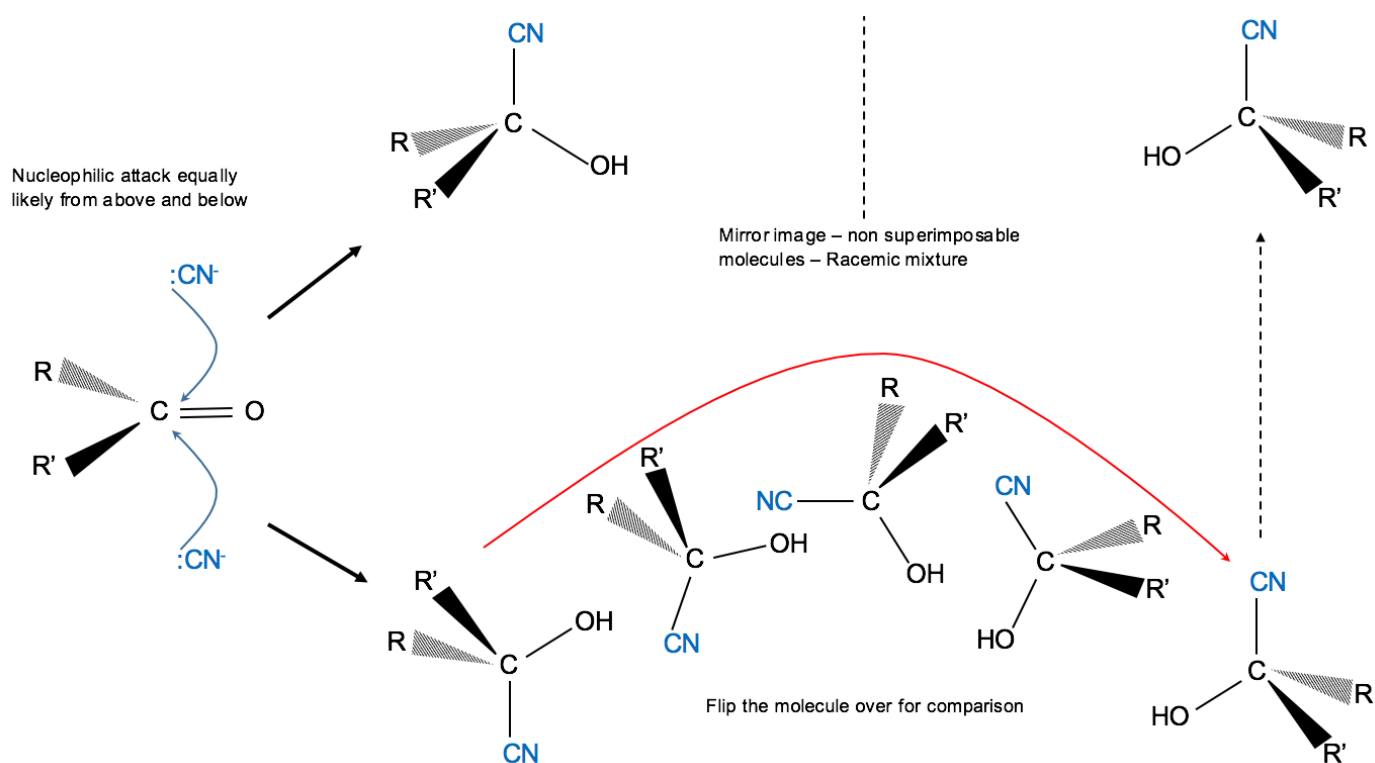
- In practise, KCN is added.
- This is because HCN is a weak acid (partially dissociates) giving a low  $[\text{CN}^-]$

## Racemic mixtures of hydroxynitriles:

- Aldehydes and ketones are planar molecules.
- Nucleophilic attack can occur from above or below and both are equally likely.
- If the aldehyde / ketone is unsymmetrical it gives a racemic mixture.
- Attack from above gives one optical isomer, attack from below gives the the other:

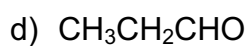
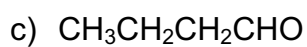
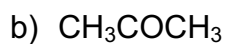
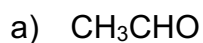


## With an aldehyde / ketone



**Questions:**

1) The reactions of aldehydes and ketones to hydroxynitriles are carried out using KCN followed by HCN. Write balanced chemical equations for the following when they react with this mixture.



2) Draw the mechanism for the reaction in 1a)

3) Draw the mechanism for the reduction of 1b)

4) Which of the following aldehydes and ketones will produce a racemic mixture when reacted with acidified KCN?

a)  $\text{CH}_3\text{CHO}$

b)  $\text{CH}_3\text{COCH}_3$

c)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$

d)  $\text{CH}_3\text{CH}_2\text{CHO}$

5) a) Draw the structure of 2 – hydroxy propanitrile:

b) 2 – hydroxy propanitrile is optically active.

Draw the 3D structure of the one of the enantiomers. Label the chiral center with a \*

c) What effect would this one enantiomer have on plane polarised light? Explain your answer:

6) a) Draw the structure of butanone:

b) Butanone reacts with acidified KCN?  
Outline the mechanism of this reaction:

c) Draw the 3D structures of the enantiomers. Label the chiral center with a \*

d) What effect will this mixture of enantiomers have on plane polarised light? Explain your answer: