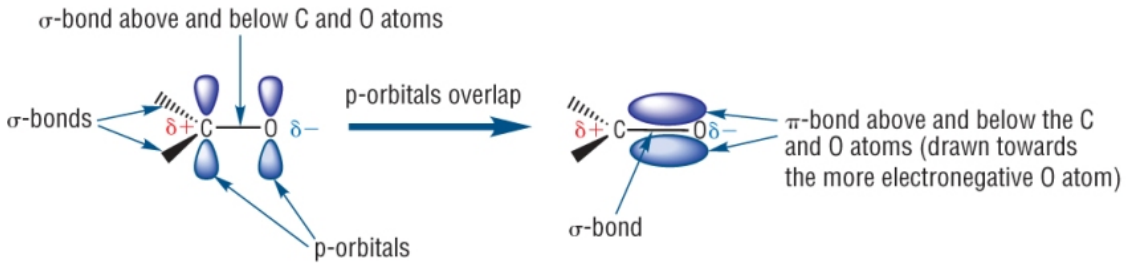
3.8 Aldehydes and ketones

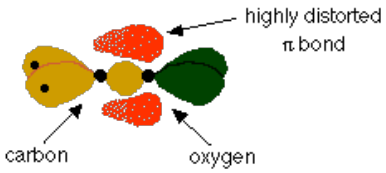
Introduction:

p's to π's

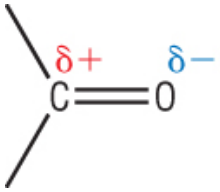
- Like the alkenes, the carbonyl group consists of a **σ bond** and a **π bond** between the carbon and oxygen:



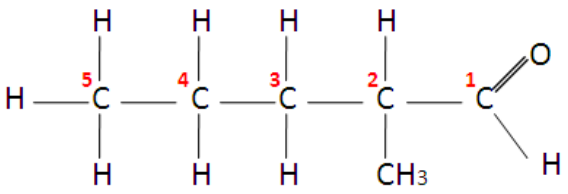
- Oxygen is more electronegative than carbon meaning that the π electrons will be highly distorted towards the oxygen atom as shown above.



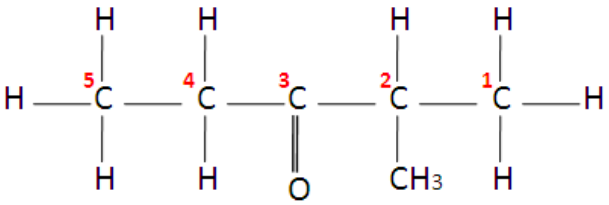
- This sets up a permanent dipole across the C=O bond:



Naming aldehydes and ketones:



2-Methylpentanal

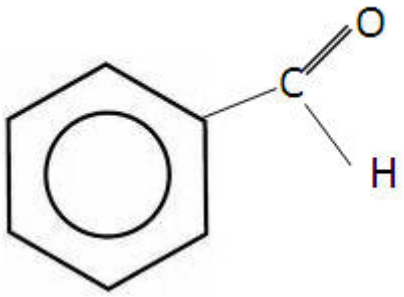


2-methylpentan-3-one

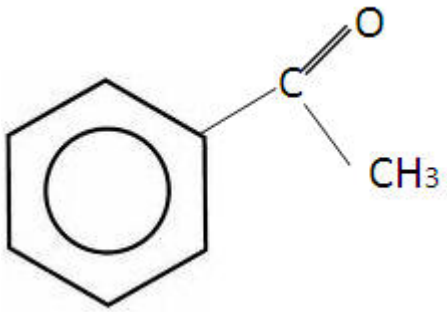
- In aldehydes, the aldehyde carbon always starts at 1.
- In ketones, the ketone (or carbonyl group) is always counted to give it the smallest possible number.

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
$CH_3CH_2CH_2CH_2CHO$	
$CH_3COCH_2CH_3$	
$(CH_3)_2CHCH_2CH_2COCH_3$	

- Draw the structure of the following:

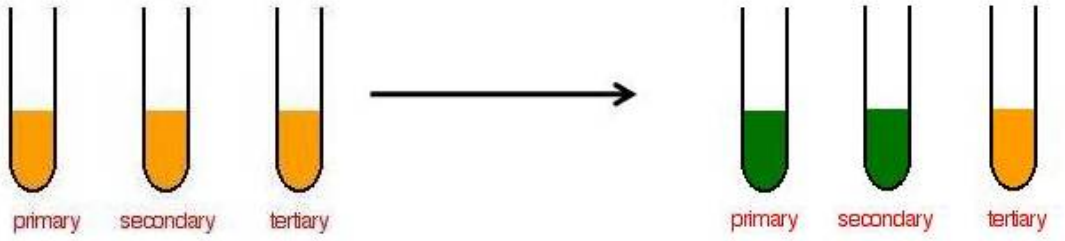
Alcohol	Structural formula	Skeletal formula
Propanone		
Pentanal		
Hexan – 3 – one		

- Complete the table below for pentanal

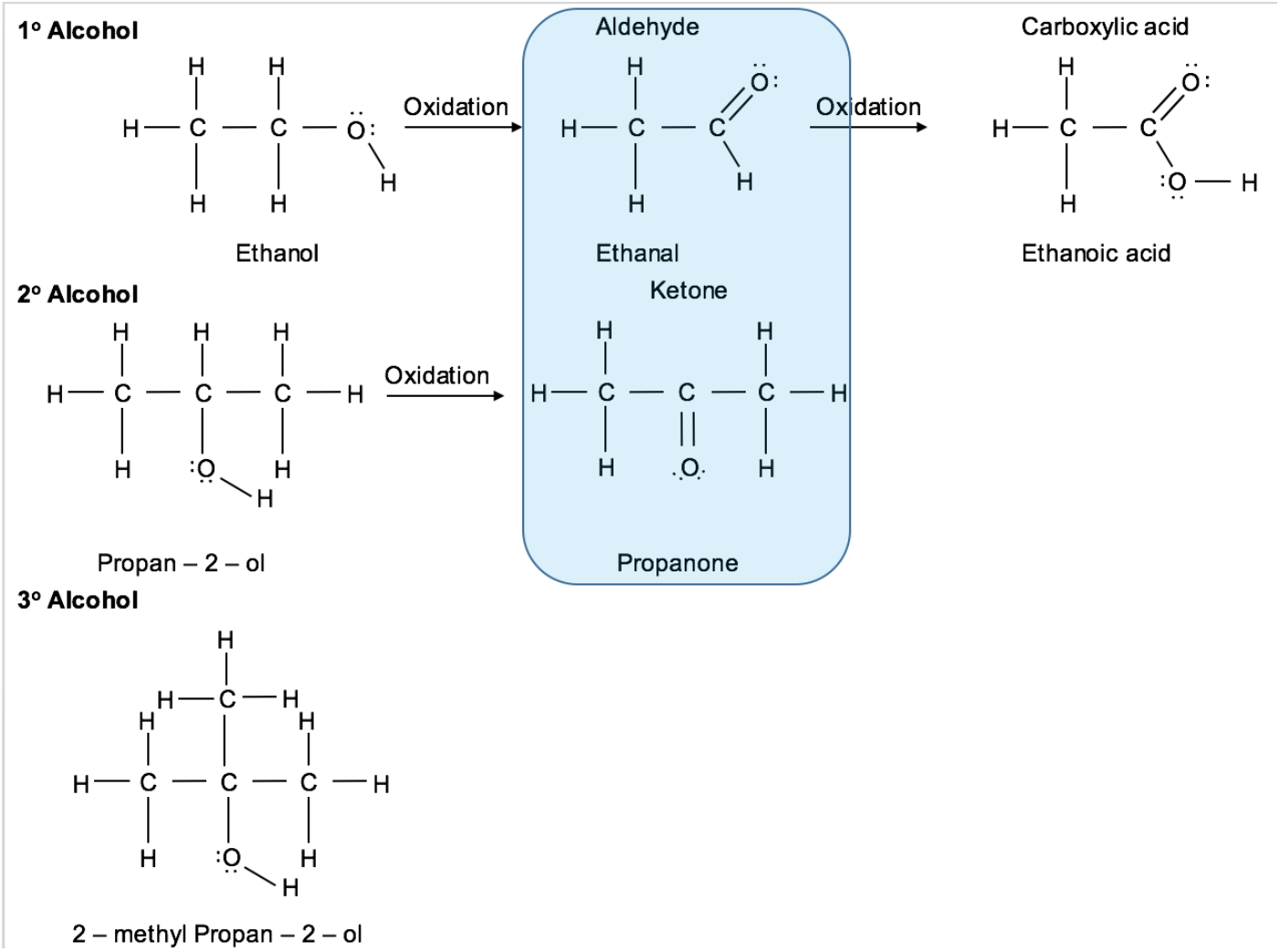
Structural formula	Functional group Isomer	Chain Isomer

A recap – Oxidation forming aldehydes and ketones:

- Aldehydes and ketones are made by the oxidation of 1^{o} and 2^{o} 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, $Ag(NH_3)_2^+$**

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

Chemical reactions

Organic: Aldehyde is oxidised to a carboxylic acid

$$CH_3CHO + [O] \rightarrow CH_3COOH$$

Reagent: Silver ions are reduced to silver

$$\underset{\text{Colourless}}{Ag(NH_3)_2^{+}{}_{(aq)}} + e^- \rightarrow \underset{\text{Silver ppt}}{Ag_{(s)}} + 2NH_{3(aq)}$$

2) **Fehling's solution –**

Reagents **$CuSO_4$ / NaOH / Warm**

Observations **Aldehyde Red precipitate**
Ketone No reaction

Chemical reactions

Organic: Aldehyde is oxidised to a carboxylic acid

$$CH_3CHO + [O] \rightarrow CH_3COOH$$

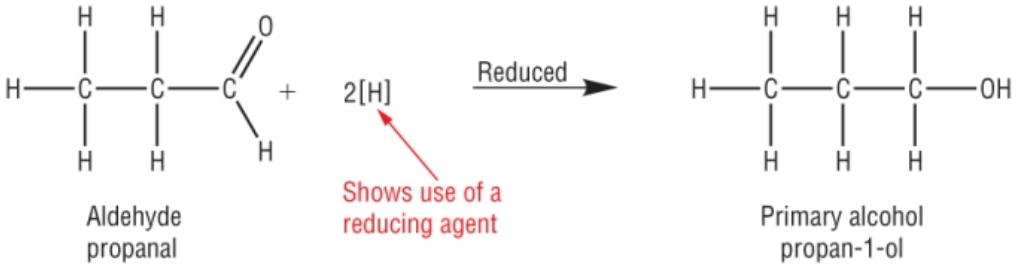
Reagent: Cu^{2+} ions are reduced to Cu^+

$$Cu^{2+}{}_{(aq)} + e^- \rightarrow Cu^+{}_{(s)}$$

Reducing aldehydes and ketones

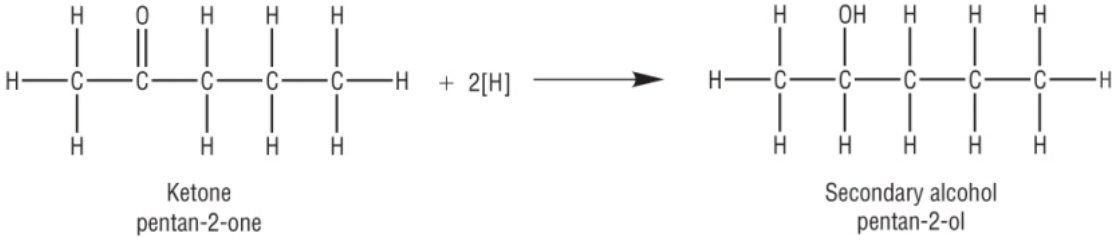
- Aldehydes and ketones can be reduced back to the primary or secondary alcohol.
- Reducing agent used is sodium tetrahydidoborate (III), $NaBH_4$.
- The reaction(s) are complex so we use [H] in the equation.

Reduction of aldehydes:



CH_3CH_2CHO + 2[H] → $CH_3CH_2CH_2OH$

Reduction of ketones:



$CH_3COCH_2CH_2CH_3$ + 2[H] → $CH_3CH(OH)CH_2CH_2CH_3$

Questions:

1) Name the following molecules:
   a. CH_3CHO b. CH_3COCH_3 c. $(CH_3)_2CHCH_2CHO$

   d. $CH_3CH_2CH_2CHO$ e. $CH_3CH_2COCH_2CH_3$ f. CH_3CH_2CHO

2) Draw, classify and name the alcohols made from the reduction of the following
   a. CH_3CHO b. CH_3COCH_3 c. $(CH_3)_2CHCH_2CHO$

   d. $CH_3CH_2CH_2CHO$ e. $CH_3CH_2COCH_2CH_3$ f. CH_3CH_2CHO

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

a. CH_3CHO b. CH_3COCH_3 c. $(CH_3)_2CHCH_2CHO$

d. $CH_3CH_2CH_2CHO$ e. $CH_3CH_2COCH_2CH_3$ f. CH_3CH_2CHO

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?

a. CH_3CHO b. CH_3COCH_3 c. $(CH_3)_2CHCH_2CHO$

d. $CH_3CH_2CH_2CHO$ e. $CH_3CH_2COCH_2CH_3$ f. CH_3CH_2CHO

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 $NaBH_4$. Write balanced chemical equations for the following. Use [H] as the reducing agent.

a) CH_3CHO

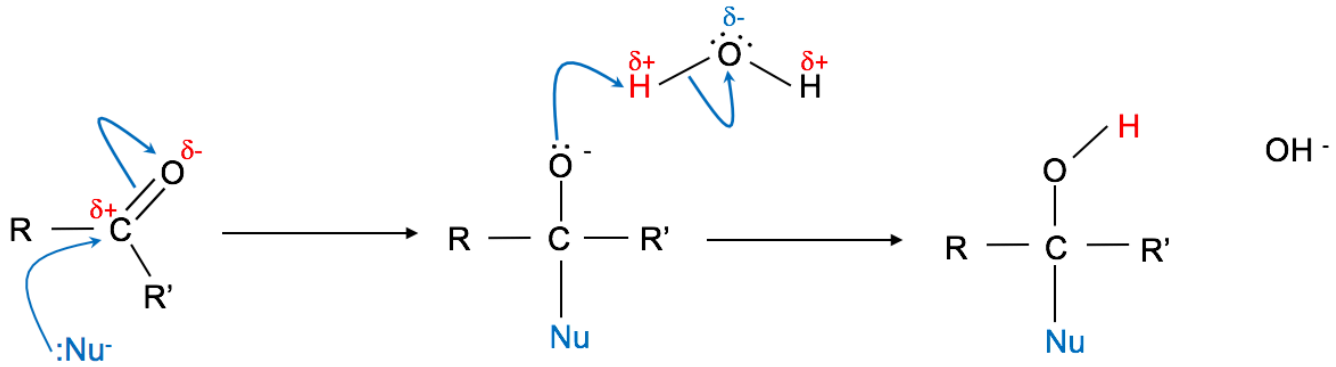
b) CH_3COCH_3

c) $CH_3CH_2CH_2CHO$

d) CH_3CH_2CHO

Nucleophilic addition reactions:

General:



Aldehyde / Ketone

- The nucleophile and is attracted to the **δ+** carbon in the carbonyl group.

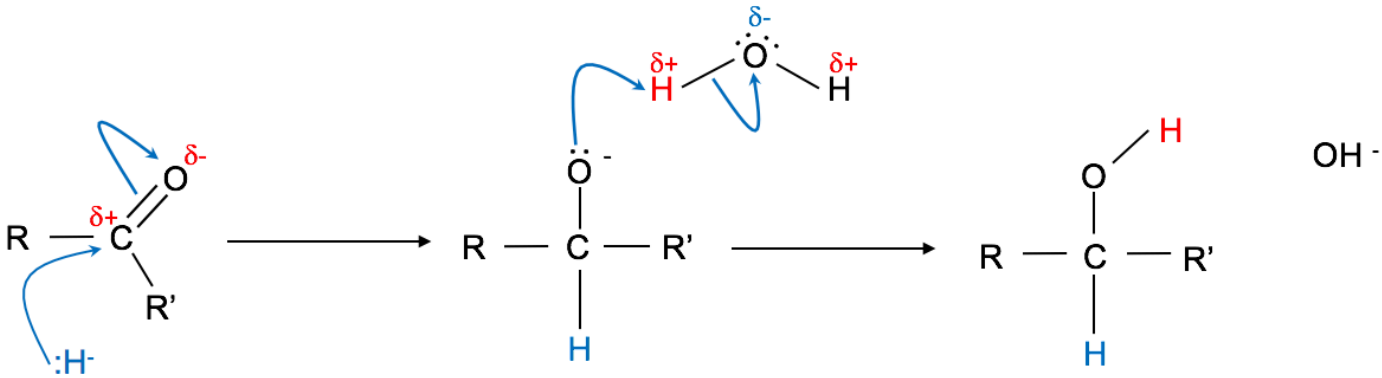
1) Reduction

CH_3CHO + 2[H] → CH_3CH_2OH

Conditions: $NaBH_4$ / Aqueous (water) - a source of hydride ions, H^- then H_2O

- This is the nucleophile and is attracted to the **δ+** carbon in the carbonyl group.

The Mechanism:

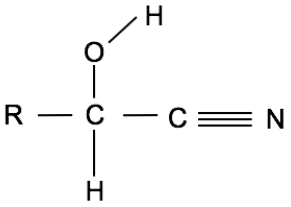


Aldehyde
or
Ketone

1° Alcohol
or
2° Alcohol

2) Hydroxynitriles

General formula:



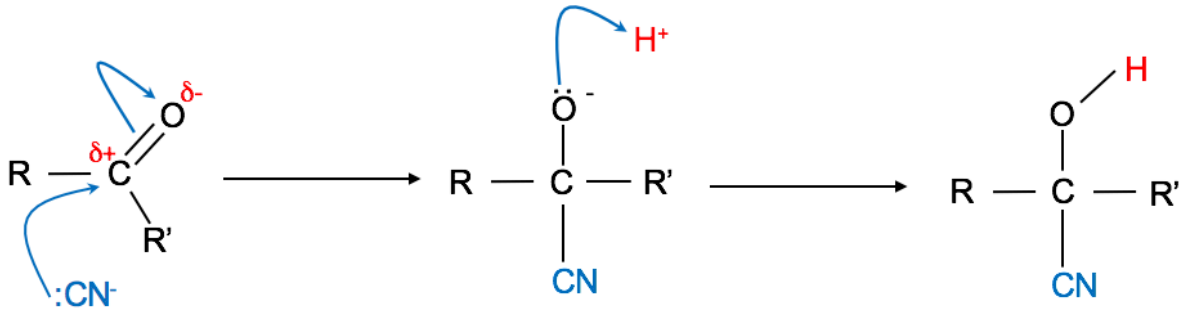
Formation:

$$CH_3CHO_{(aq)} + HCN_{(aq)} \rightarrow CH_3CH(OH)CN_{(aq)}$$

Conditions: KCN followed by dilute acid (HCl) – This produces HCN (as CN^- and H^+)

- **CN^-** is the nucleophile and is attracted to the **δ+** carbon in the carbonyl group.

The Mechanism:

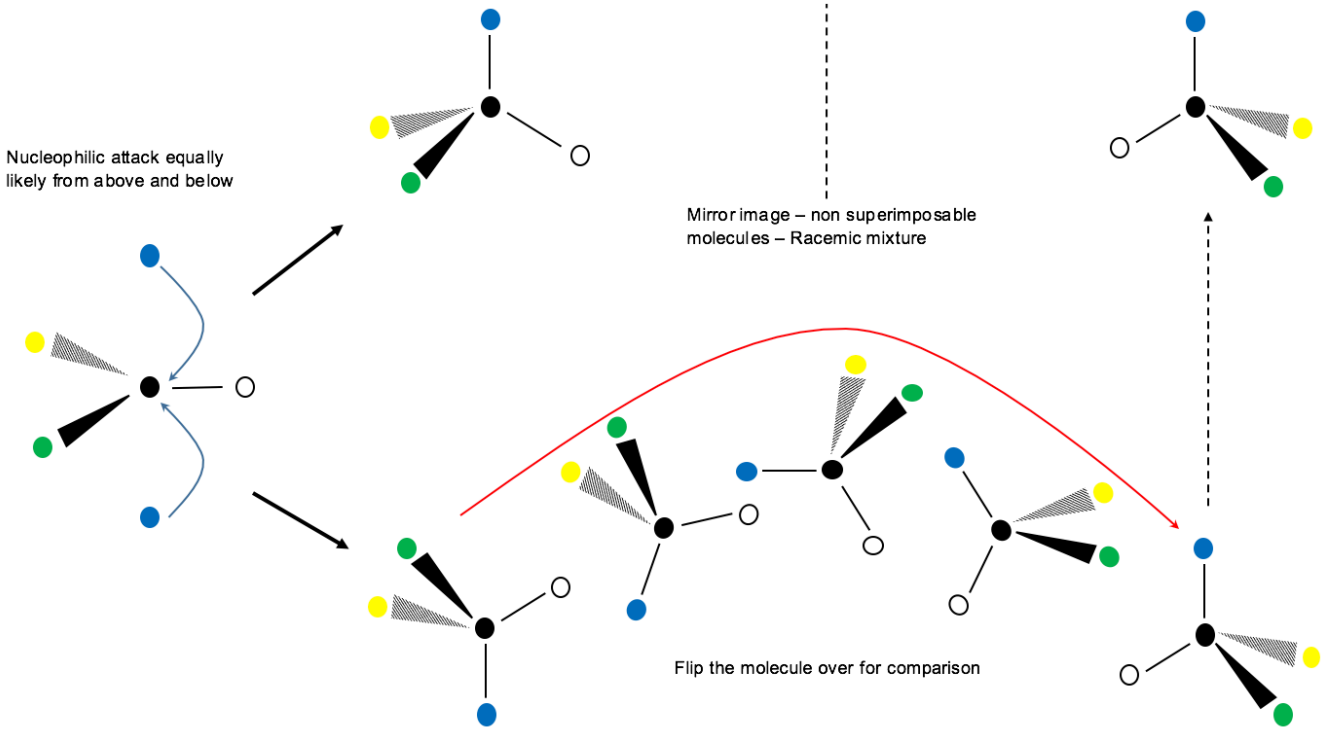


Aldehyde / Ketone Hydroxynitrile

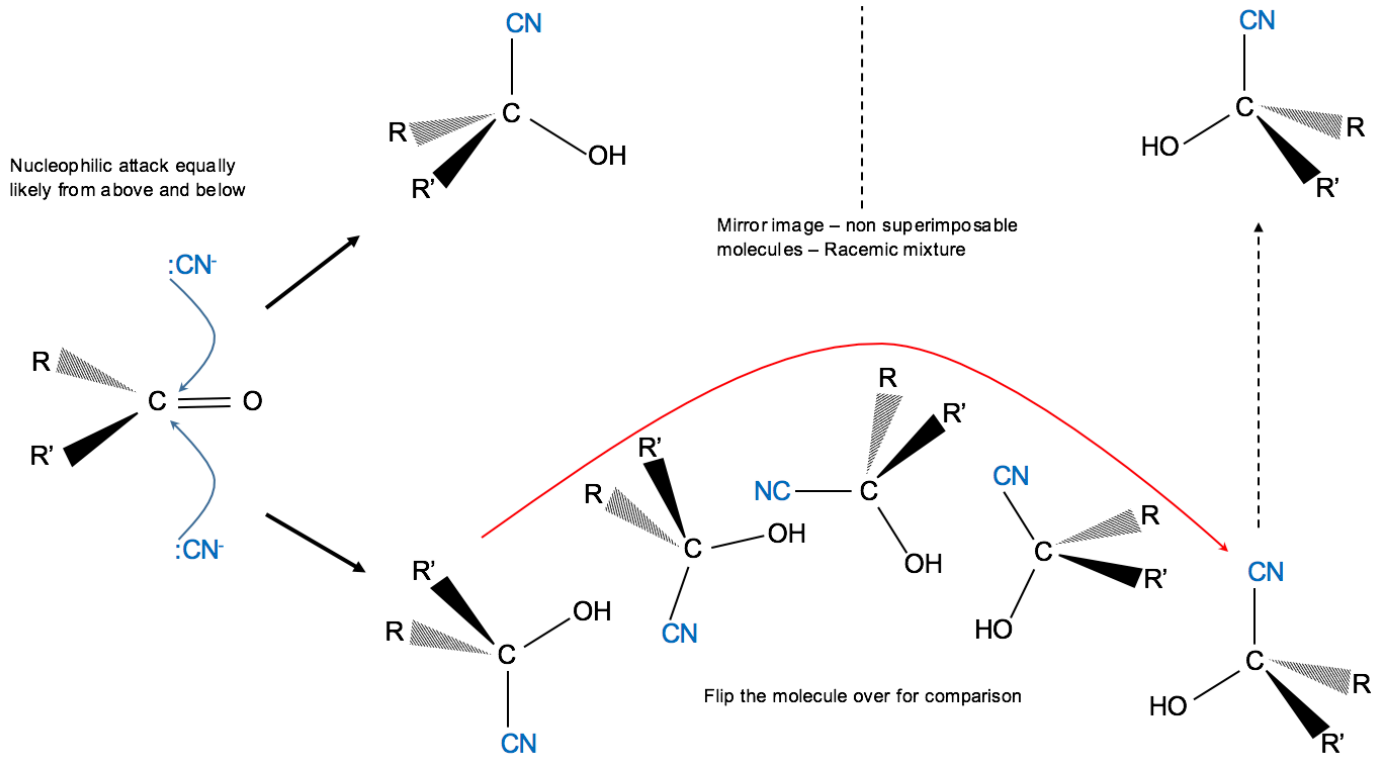
- In practise, KCN is added.
- This is because HCN is a weak acid (partially dissociates) giving a low [CN^-]

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 other:



With an aldehyde / ketone



Questions:

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

   a) CH_3CHO

   b) CH_3COCH_3

   c) $CH_3CH_2CH_2CHO$

   d) CH_3CH_2CHO

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) CH_3CHO

   b) CH_3COCH_3

   c) $CH_3CH_2CH_2CHO$

   d) CH_3CH_2CHO

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: