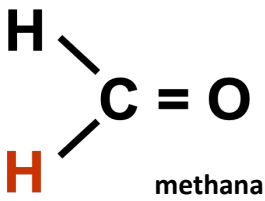
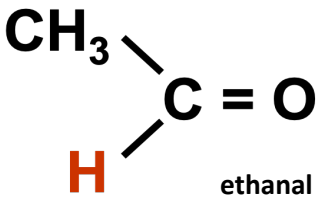
Carbonyl Compounds

These contain the C=O double bond.
In aldehydes, the carbonyl group is at the end of the carbon chain.

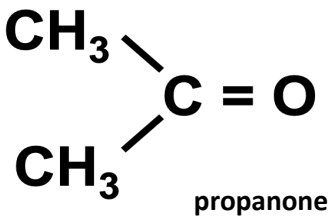


methanal

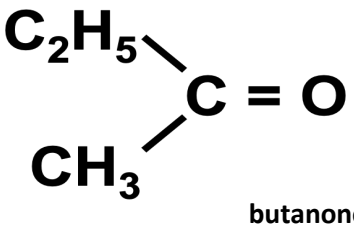


ethanal

In ketones, the carbonyl group is joined to C atoms on each side.



propanone



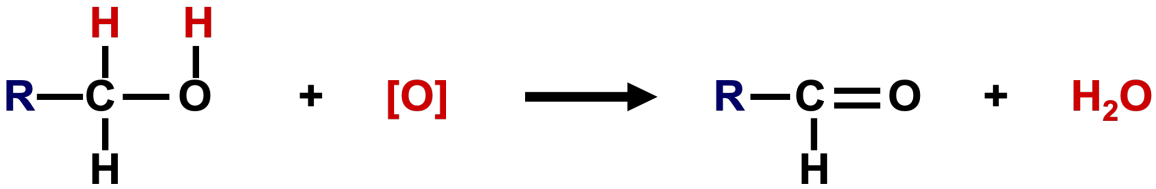
butanone

Reactions of carbonyl compounds (see AS Chemistry)

Oxidation

On **gentle** heating, **primary alcohols** are oxidised to **aldehydes (RCHO)** that can be **distilled off** as they are formed.

ethanol + [O] $\xrightarrow{K_2Cr_2O_7/H_2SO_4}$ ethanal + water



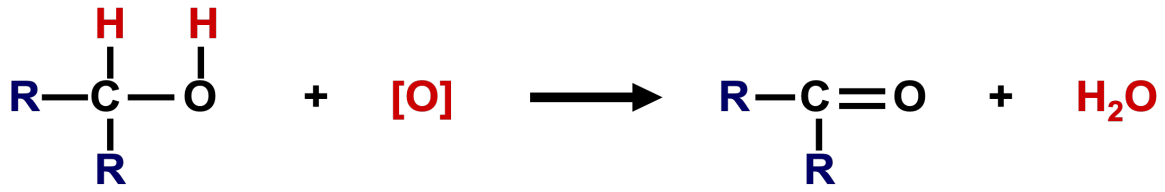
Under reflux with **excess** acidified dichromate, aldehydes are oxidised to carboxylic acids, RCOOH,

ethanal + [O] → ethanoic acid

CH_3CHO + [O] → CH_3COOH

Secondary alcohols produce **ketones** (RCOR') on gentle heating with acidified dichromate.
No further oxidation is possible.

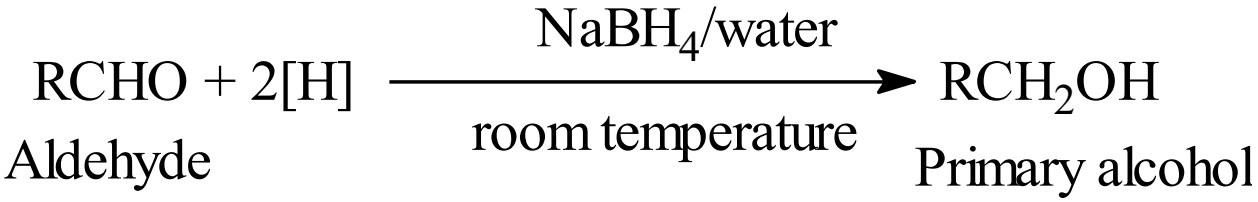
propan-2-ol + [O] → propanone + water



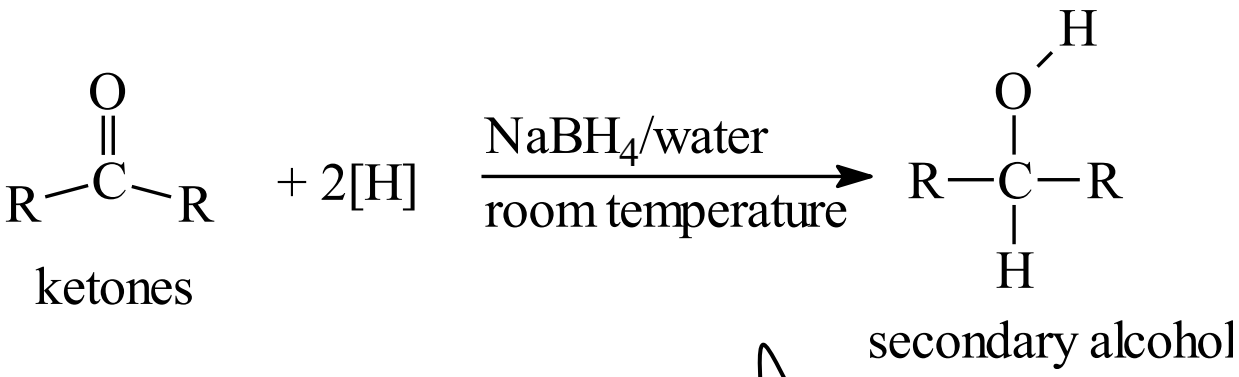
Reduction

Using sodium borohydride ($Na\ BH_4$). Conditions: dissolve in water and warm gently.

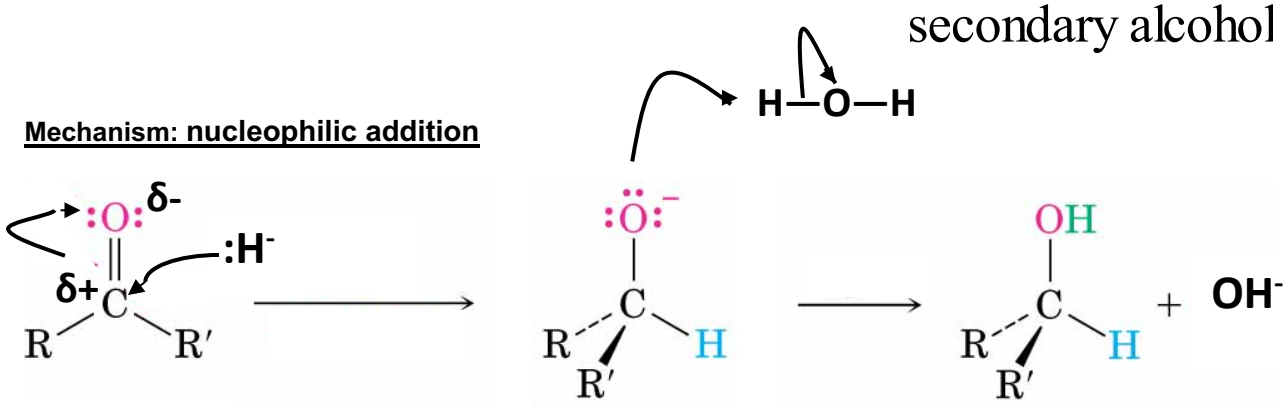
Aldehydes are reduced to 1ʸ alcohols:



Ketones to 2ʸ alcohols



Mechanism: nucleophilic addition

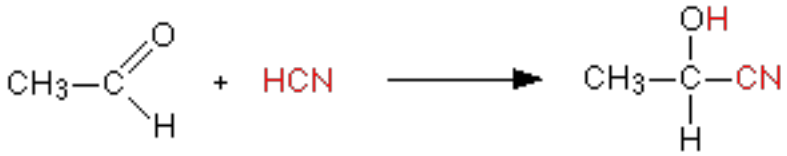


The nucleophile is $:H^-$, the hydride ion.

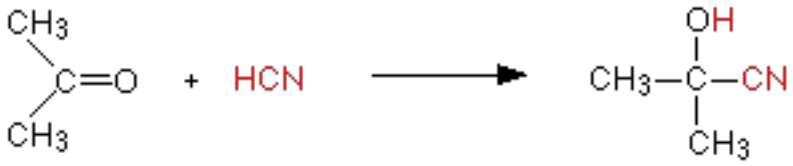
Reaction with KCN

Hydrogen cyanide adds across the carbon-oxygen double bond in aldehydes and ketones to produce compounds known as hydroxynitriles. The reaction isn't normally done using hydrogen cyanide itself, because this is an extremely poisonous gas. Instead, the aldehyde or ketone is mixed with a solution of sodium or potassium cyanide in water to which a little sulphuric acid has been added.

For example, with ethanal (an aldehyde) you get 2-hydroxypropanenitrile:



With propanone (a ketone) you get 2-hydroxy-2-methylpropanenitrile:

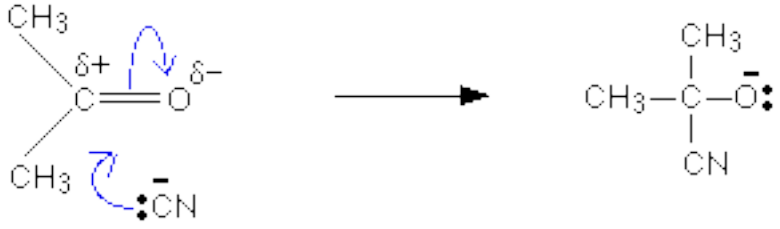


Naming: the longest carbon chain must include the –CN group. The carbon with the nitrogen attached is always counted as number 1.

All aldehydes will form a racemic mixture in this way. Unsymmetrical ketones will as well. (A ketone can be unsymmetrical in the sense that there is a different alkyl group either side of the carbonyl group.) What matters is that the product molecule must have four different groups attached to the carbon, which was originally part of the carbon-oxygen double bond.

Mechanism:

The mechanism for the addition of HCN to propanone
In the first stage, there is a nucleophilic attack by the cyanide ion on the slightly positive carbon atom.

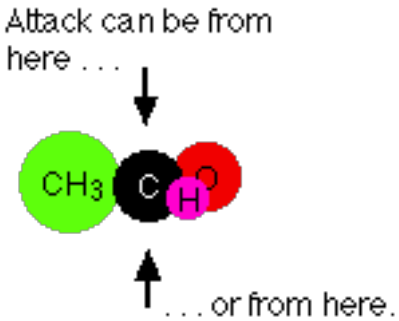


The negative ion formed then picks up a hydrogen ion from somewhere - for example, from a hydrogen cyanide molecule.

The hydrogen ion could also come from the water present in the slightly acidic solution.

When 2-hydroxypropanenitrile is made in this last mechanism, it occurs as a *racemic mixture* - a 50/50 mixture of two optical isomers.

The reason for the formation of equal amounts of two isomers lies in the way the ethanal gets attacked. Ethanal is a planar molecule, and attack by a cyanide ion will either be from above the plane of the molecule, or from below. There is an equal chance of either happening.



Attack from one side will lead to one of the two isomers, and attack from the other side will lead to the other.

HCN is toxic and is particularly dangerous as some people can only detect its odour at levels that may be lethal.

Test for identifying a carbonyl compound

When a solution of **2,4-dinitrophenylhydrazine** is added to an aldehyde or ketone an orange precipitate of a 2,4-dinitrophenylhydrazone is formed. This reaction is unique to aldehydes and ketones

The precipitates can be recystallised and the melting point of the solid used to identify the aldehyde or ketone by comparison with values for known compounds.

Test to distinguish between aldehydes and ketones

Aldehydes can easily be oxidised, ketones cannot. So **Tollens' reagent** (ammoniacal silver nitrate solution) reacts on warming with an aldehyde (but not a ketone) to form **a silver mirror.**

$CH_3CHO + 2Ag^+ + H_2O \rightarrow CH_3COOH + 2Ag + 2H^+$

ethanal ethanoic acid silver

This equation may simplified to in an examination to:

$CH_3CHO + [O] \rightarrow CH_3COOH$