

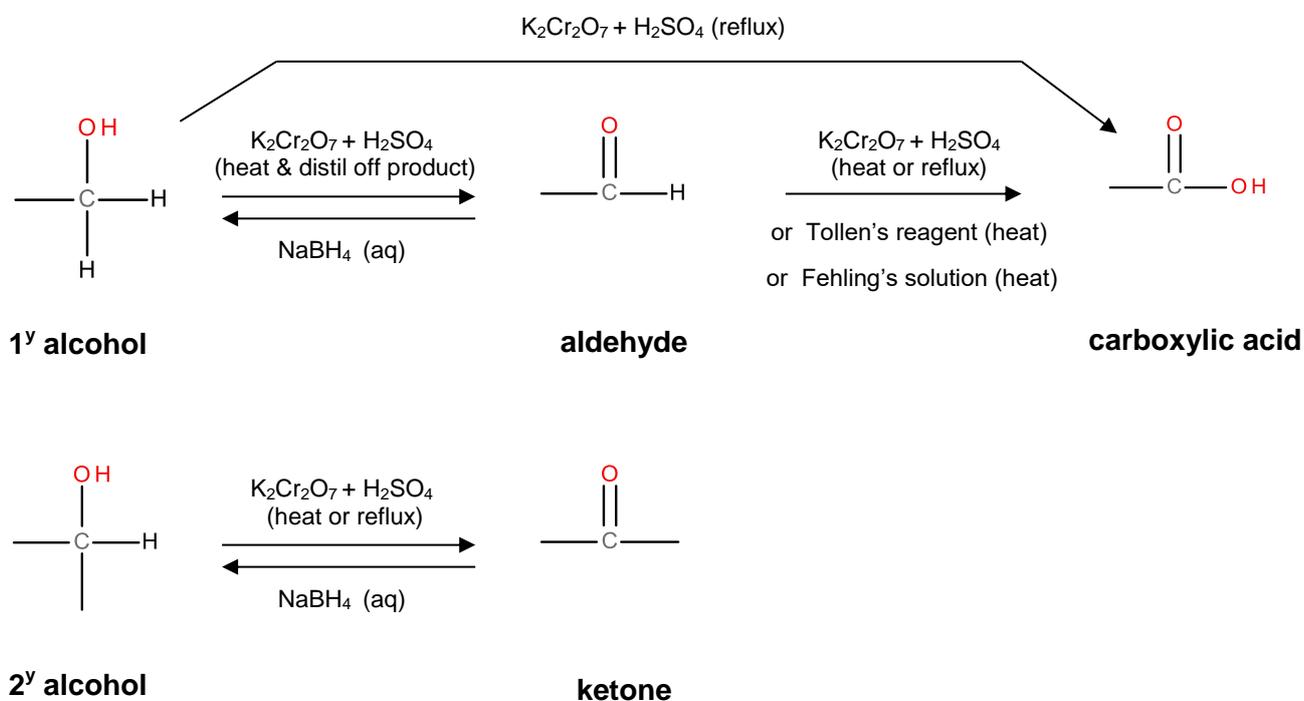
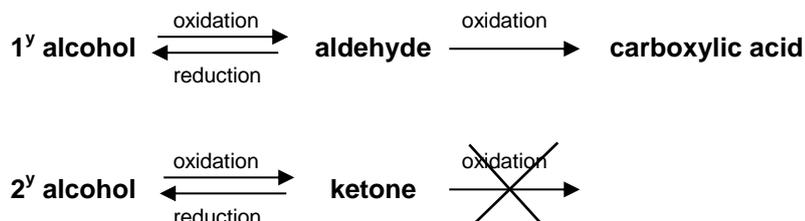


# REACTIONS OF ALDEHYDES & KETONES

## OXIDATION & REDUCTION

Aldehydes can be oxidised by mild oxidising agents to carboxylic acids, but ketones are not oxidised by these oxidising agents as a C-C would have to be broken.

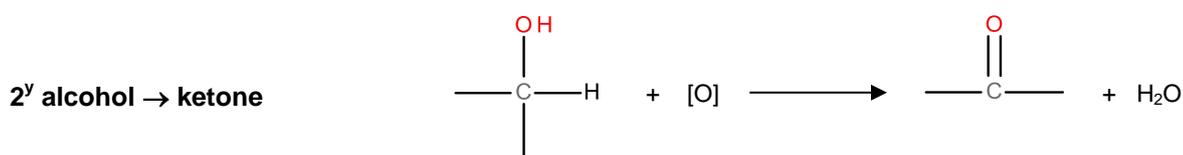
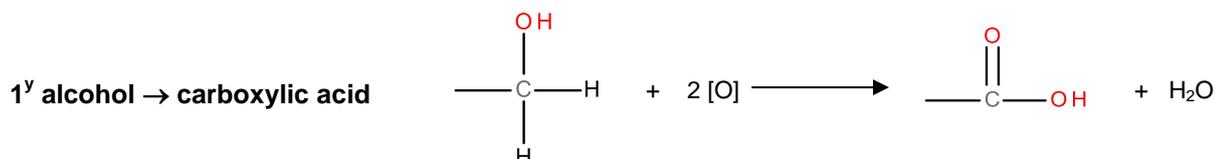
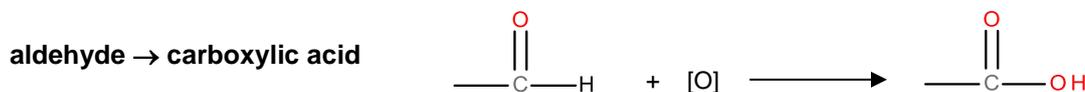
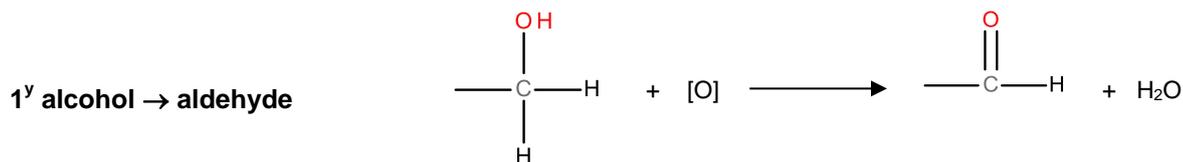
Aldehydes and ketones can both be reduced to alcohols (primary alcohols to aldehydes, ketones to secondary alcohols).



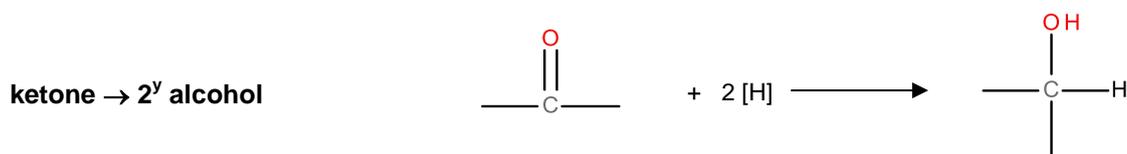
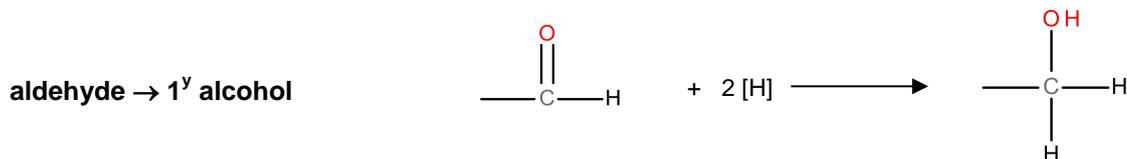
### Important notes about the reactions

- $\text{K}_2\text{Cr}_2\text{O}_7$  &  $\text{H}_2\text{SO}_4$**
- **Orange**  $\text{Cr}_2\text{O}_7^{2-}$  ions (Cr +6) are themselves reduced to **green**  $\text{Cr}^{3+}$  ions (Cr +3) as they oxidise the alcohol / aldehyde
  - If you wish to oxidise a primary alcohol and prevent oxidation of the aldehyde to a carboxylic acid, the aldehyde is removed by distillation as it is formed (the aldehyde has a lower boiling point than the alcohol as it does not have hydrogen bonding)
- Tollen's reagent**
- Tollen's reagent contains  $[\text{Ag}(\text{NH}_3)_2]^+$  ions (Ag +1) which are reduced to a **silver mirror** (Ag 0) as it oxidises the aldehyde to a carboxylic acid.
  - This reaction is used as a simple test to distinguish aldehydes from ketones
- Fehling's solution**
- Fehling's solution, which is a **blue solution**, contains  $\text{Cu}^{2+}$  ions (Cu +2) which are reduced to a **brick-red precipitate** of  $\text{Cu}_2\text{O}$  (Cu +1) as it oxidises the aldehyde to a carboxylic acid.
  - This reaction is used as a simple test to distinguish aldehydes from ketones

## OXIDATION equations



## REDUCTION equations



## TASK

Write balanced equations for the following reactions. Always **draw structural formulas** of organic compounds and **name the organic product**. Write *no reaction* if there is no reaction!

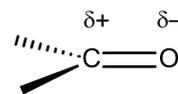
- 1) propanal + NaBH<sub>4</sub>
- 2) propan-1-ol + H<sub>2</sub>SO<sub>4</sub> / K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> distilling off the product
- 3) butanal + Tollen's reagent with heating
- 4) propanone + Fehling's solution with heating
- 5) butanone + NaBH<sub>4</sub>
- 6) methylpropan-2-ol + H<sub>2</sub>SO<sub>4</sub> / K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> refluxing
- 7) methylpropan-1-ol + H<sub>2</sub>SO<sub>4</sub> / K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> refluxing
- 8) 3-methylbutanal + H<sub>2</sub>SO<sub>4</sub> / K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> refluxing

## NUCLEOPHILIC ADDITION

The C=O is polar with the C being  $\delta+$  (due to O being much more electronegative than C). This means that the C is susceptible to attack by nucleophiles (electron pair donors).

The three atoms joined to the C of the C=O group are arranged in a trigonal planar shape, and so the C, O and the other two atoms joined to the C are in the same plane.

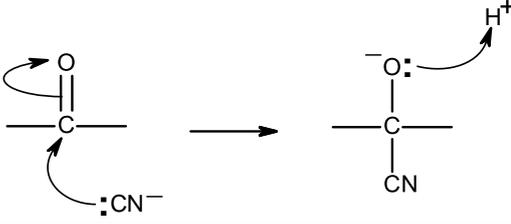
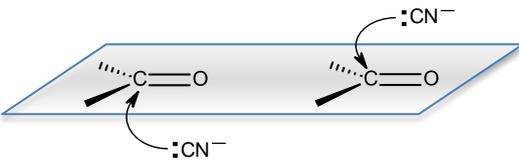
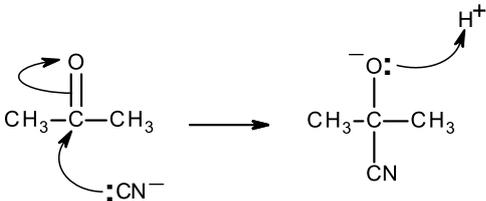
As there is a double bond, reagents can add across the double bond.



### NUCLEOPHILIC ADDITION 1 – reduction

<b>Reagent</b>	NaBH <sub>4</sub>
<b>Conditions</b>	aqueous
<b>What happens</b>	Two H atoms add onto the C=O double bond, one onto the C and one onto the O
<b>Products</b>	Primary alcohols (from aldehydes)      Secondary alcohols (from ketones)
<b>Overall equation</b>	$\begin{array}{c} \text{O} \\    \\ \text{---C---} \end{array} + 2[\text{H}] \longrightarrow \begin{array}{c} \text{OH} \\   \\ \text{---C---} \\   \\ \text{H} \end{array}$
<b>Mechanism</b>	<p style="text-align: center;"><b>nucleophilic addition</b></p>
<b>Note</b>	The NaBH <sub>4</sub> acts as a source of hydride (H <sup>-</sup> ions), while the water then provides H <sup>+</sup> ions
<b>Example 1</b>	<p>e.g. ethanal + NaBH<sub>4</sub></p> $\text{CH}_3\text{---}\begin{array}{c} \text{O} \\    \\ \text{C} \end{array}\text{---H} + 2[\text{H}] \longrightarrow \text{CH}_3\text{---}\begin{array}{c} \text{OH} \\   \\ \text{C} \end{array}\text{---H} \\   \\ \text{H}$ <p><b>nucleophilic addition</b></p>
<b>Example 2</b>	e.g. propanone + NaBH <sub>4</sub>

## NUCLEOPHILIC ADDITION 2 – addition of HCN

<b>Reagent</b>	KCN followed by dilute acid
<b>Conditions</b>	aqueous
<b>What happens</b>	CN adds onto the C of the C=O; H adds onto the O of the C=O
<b>Products</b>	Hydroxynitriles
<b>Overall equation</b>	$\begin{array}{c} \text{O} \\    \\ \text{---C---} \end{array} + \text{HCN} \longrightarrow \begin{array}{c} \text{OH} \\   \\ \text{---C---} \\   \\ \text{CN} \end{array}$
<b>Mechanism</b>	<p style="text-align: center;"><b>nucleophilic addition</b></p> 
<b>Note</b>	<p>The CN<sup>-</sup> ions come from the KCN. The acid provides the H<sup>+</sup> ions.</p> <p>You will not do this in the lab as the KCN (and HCN that may be formed) are very toxic.</p> <p>For many aldehydes and ketones, the hydroxynitrile produced will be formed as a mixture of enantiomers as most contain chiral C atoms.</p> <p>Due to the planar nature of the C=O group, the CN<sup>-</sup> ion has an equal chance of attaching the δ<sup>+</sup> C from above or below and so a racemic mixture (50/50 mixture of the two enantiomers) would be formed.</p> 
<b>Example 3</b>	<p>e.g. propanone + KCN then acid</p> $\text{CH}_3\text{---}\overset{\text{O}}{\parallel}\text{---}\text{C}\text{---}\text{CH}_3 + \text{HCN} \longrightarrow \begin{array}{c} \text{OH} \\   \\ \text{CH}_3\text{---C---CH}_3 \\   \\ \text{CN} \end{array}$ <p><b>nucleophilic addition</b></p> 
<b>Example 4</b>	e.g. propanal + KCN then acid