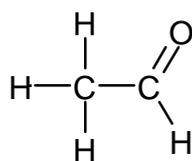


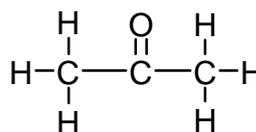
## Carbonyls: Aldehydes and Ketones

Carbonyls are compounds with a C=O bond. They can be either aldehydes or ketones



If the C=O is on the end of the chain with an H attached it is an aldehyde.  
The name will end in **-al**

CH<sub>3</sub>CHO ethanal

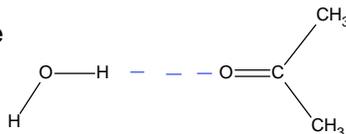


If the C=O is in the middle of the chain it is a ketone.  
The name will end in **-one**

CH<sub>3</sub>COCH<sub>3</sub> propanone

### Solubility in water

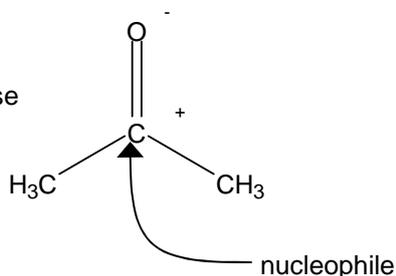
The smaller carbonyls are soluble in water because they can form hydrogen bonds with water.



Pure carbonyls cannot form hydrogen bonds. They form permanent dipole-dipole intermolecular forces between their molecules.

### Reactions of carbonyls

The C=O bond is polarised because O is more electronegative than carbon. The positive carbon atom attracts nucleophiles.



In comparison to the C=C bond in alkenes, the C=O is stronger and does not undergo addition reactions easily.

This is in contrast to the electrophiles that are attracted to the C=C.

### Oxidation reactions

Potassium dichromate K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is an oxidising agent that causes alcohols and aldehydes to oxidise.

Primary alcohol → aldehydes → carboxylic acid

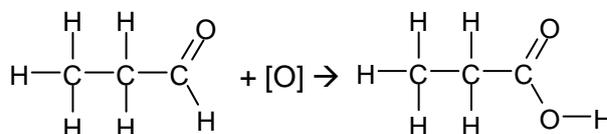
Secondary alcohol → ketones

Tertiary alcohols do not oxidise

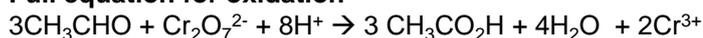
Key point: Aldehydes can be oxidised to carboxylic acids, but ketones cannot be oxidised.

### Oxidation of aldehydes

**Reaction:** aldehyde → carboxylic acid  
**Reagent:** potassium dichromate (VI) solution and dilute sulfuric acid.  
**Conditions:** heat under reflux



### Full equation for oxidation



Observation: the orange dichromate ion (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) reduces to the green Cr<sup>3+</sup> ion

Aldehydes can also be oxidised using Fehling's solution or Tollen's Reagent. These are used as tests for the presence of aldehyde groups

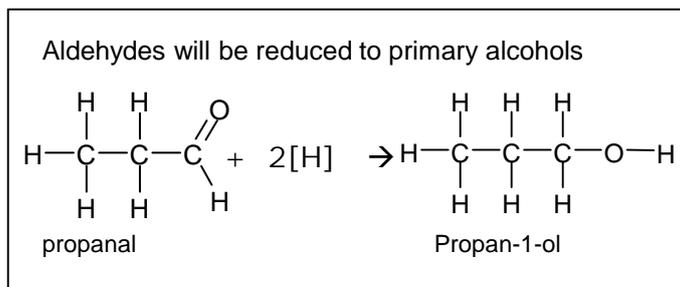
## Reduction of carbonyls

Carbonyls can be reduced back to alcohols by reducing agents. The most common reducing agent is sodium tetrahydridoborate ( $\text{NaBH}_4$ ). A more powerful reducing agent called lithium tetrahydridoaluminum ( $\text{LiAlH}_4$ ) can also be used. These reducing agents supply hydride ions  $\text{H}^-$  which attack the  $\delta^+$  Carbon in aldehydes and ketones.

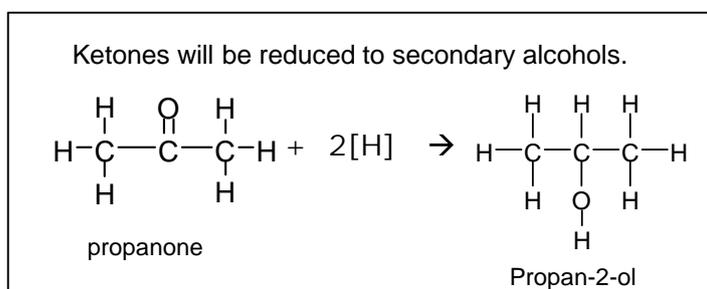
Sodium tetrahydridoborate is a white crystalline solid. It is dissolved in water or ethanol for the reaction

**Reagents:**  $\text{NaBH}_4$  in aqueous ethanol

**Conditions:** Room temperature and pressure

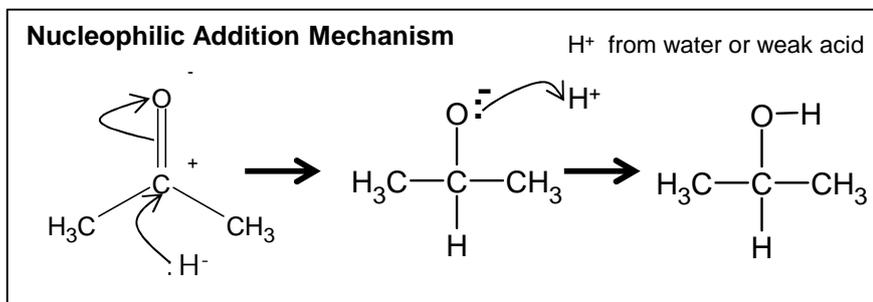


The reactions can be simplified with the use of  $[\text{H}]$  to represent the hydrogen from the reducing agent.



Lithium tetrahydridoaluminum will also reduce carbonyls. It is a more powerful reducing agent than sodium tetrahydridoborate.  $\text{LiAlH}_4$  will reduce water so cannot be dissolved in water like  $\text{NaBH}_4$ . Dry ether is the solvent used instead.

The simplified version of the nucleophilic addition reaction is shown below



$\text{NaBH}_4$  contain a source of nucleophilic hydride ions ( $\text{H}^-$ ) which are attracted to the  $\delta^+$  carbon in the  $\text{C}=\text{O}$  bond.

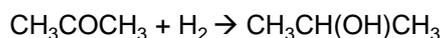
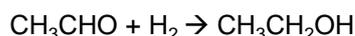
### Catalytic Hydrogenation

Carbonyls can also be reduced using catalytic hydrogenation. These are similar reactions to the reduction of alkenes to alkanes.

Reagent: hydrogen gas and nickel catalyst

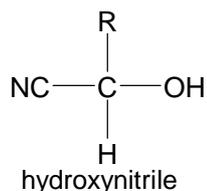
Conditions: high pressure

Example Equations



## Addition of hydrogen cyanide to carbonyls to form hydroxynitriles

Another nucleophilic addition reaction of carbonyls is with hydrogen cyanide. This reaction can be used to increase the length of the carbon chain. The product is called a **hydroxynitrile**.



We could use HCN for this reaction but it is a toxic gas that is difficult to contain.

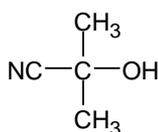
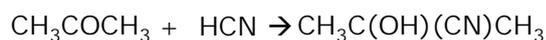
Instead we use a mixture of sodium or potassium cyanide (NaCN) and dilute sulfuric acid.

KCN/NaCN are still, however, toxic, because of the cyanide ion. The reaction is not therefore carried out in a school laboratory.

Another advantage of using KCN or NaCN is that there will be a higher concentration of the  $\text{CN}^-$  ion as these compounds will completely ionise. HCN is a weak acid and will only partially ionise

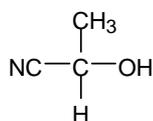
**Reaction:** carbonyl  $\rightarrow$  hydroxynitrile  
**Reagent:** sodium cyanide (NaCN) and dilute sulfuric acid.  
**Conditions:** room temperature and pressure  
**Mechanism:** nucleophilic addition

The NaCN supplies the nucleophilic  $\text{CN}^-$  ions. The  $\text{H}_2\text{SO}_4$  acid supplies  $\text{H}^+$  ions needed in second step of the mechanism

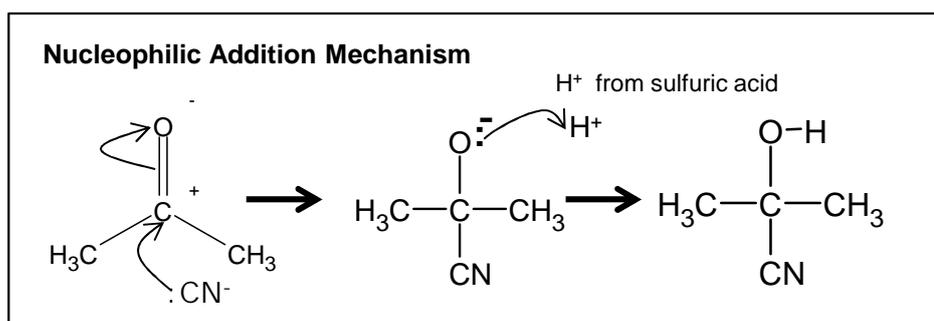


2-hydroxy-2-methylpropanenitrile

When naming hydroxynitriles the CN becomes part of the main chain.

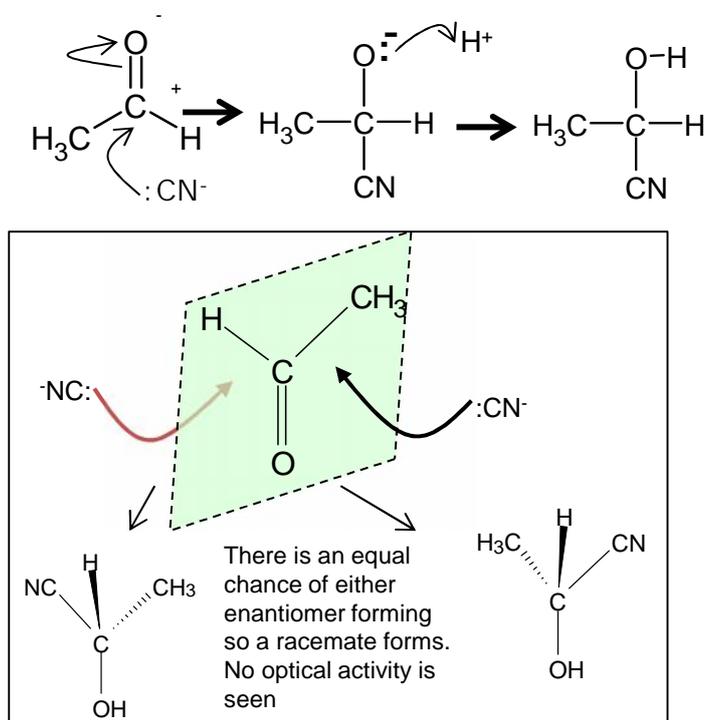


2-hydroxypropanenitrile



Nucleophilic addition of HCN to aldehydes and ketones (unsymmetrical) when the trigonal planar carbonyl is approached from both sides by the HCN attacking species: results in the formation of a racemate.

Mechanism for the reaction (drawn the same for both enantiomers)

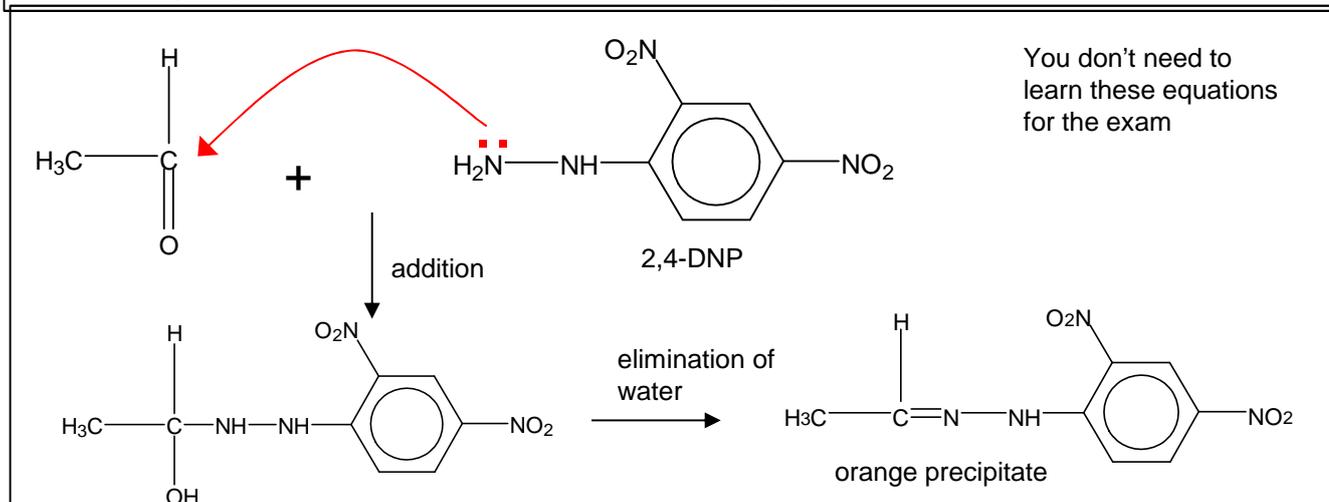


### Reaction with 2,4-dinitro phenylhydrazine

2,4-DNP reacts with both aldehydes and ketones. The product is an orange precipitate, It can be used as a test for a carbonyl group in a compound.

Use 2,4-DNP to identify if the compound is a carbonyl. Then to differentiate an aldehyde from a ketone use Tollens' reagent.

The melting point of the crystal formed can be used to help identify which carbonyl was used. Take the melting point of orange crystals product from 2,4-DNP. Compare melting point with known values in database



## Functional group tests for an aldehyde

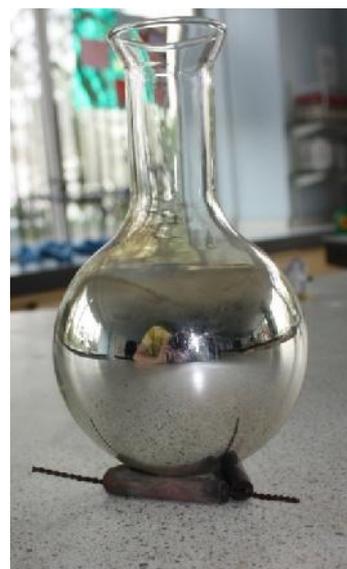
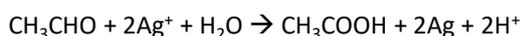
### Tollen's Reagent

**Reagent:** Tollens' Reagent formed by mixing aqueous ammonia and silver nitrate. The active substance is the complex ion of  $[\text{Ag}(\text{NH}_3)_2]^+$ .

**Conditions:** heat gently

**Reaction:** **aldehydes only** are oxidised by Tollens' reagent into a carboxylic acid and the silver(I) ions are reduced to silver atoms

**Observation:** with aldehydes, a silver mirror forms coating the inside of the test tube. Ketones result in no change.



### Tollens' reagent method

Place 1 cm<sup>3</sup> of silver nitrate solution in each of two clean boiling tubes. Then add one drop of sodium hydroxide solution to form a precipitate of silver oxide. Add ammonia solution dropwise until a clear, colourless solution is formed. Add a few drops of the unknown and leave in the water bath for a few minutes.

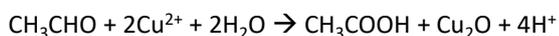
### Fehling's solution

**Reagent:** Fehling's Solution containing blue  $\text{Cu}^{2+}$  ions.

**Conditions:** heat gently

**Reaction:** **aldehydes only** are oxidised by Fehling's Solution into a carboxylic acid and the copper (II) ions are reduced to copper(I) oxide.

**Observation:** **Aldehydes:** Blue  $\text{Cu}^{2+}$  ions in solution change to a red precipitate of  $\text{Cu}_2\text{O}$ . **Ketones do not react**



### Fehling's solution method

Place 1 cm<sup>3</sup> of Fehling's A into each of two boiling tubes, and then add Fehling's B until the blue precipitate redissolves. Add a few drops of the unknown and leave in the water bath for a few minutes.

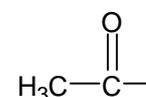
## Reaction of carbonyls with iodine in presence of alkali

**Reagents:** Iodine and sodium hydroxide

**Conditions:** warm very gently

The product  $\text{CHI}_3$  is a yellow crystalline precipitate with an antiseptic smell.

Only carbonyls with a methyl group next to the  $\text{C}=\text{O}$  bond will do this reaction. Ethanal is the only aldehyde that reacts. More commonly this is used to test for methyl ketones.



This reaction is called the Iodoform test

