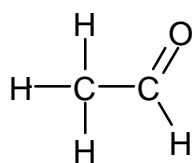


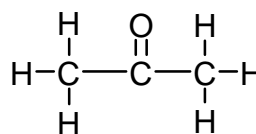
6.1.2 Carbonyl Compounds

Carbonyls: Aldehydes and Ketones

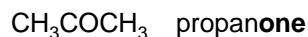
Carbonyls are compounds with a C=O bond. They can be either aldehydes or ketones



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**

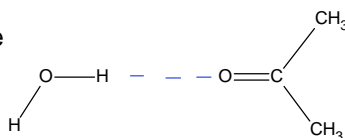


If the C=O is in the middle of the chain it is a ketone.
The name will end in **-one**



Solubility in water

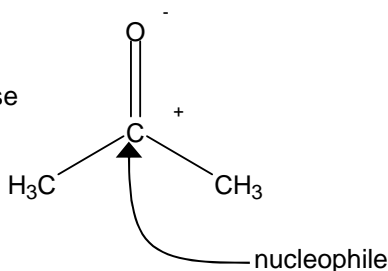
The smaller carbonyls are soluble in water because they can form hydrogen bonds with water.



Pure carbonyls cannot hydrogen bond, but bond instead by permanent dipole forces.

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

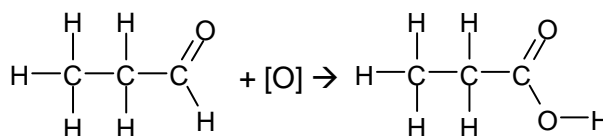
Potassium dichromate K₂Cr₂O₇ is an oxidising agent that causes alcohols and aldehydes to oxidise.

Primary alcohol → aldehydes → carboxylic acid
Secondary alcohol → ketones
Tertiary alcohols do not oxidise

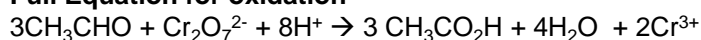
Key point: Aldehydes can be oxidised to carboxylic acids, but ketones cannot be oxidised.

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 (Cr₂O₇²⁻) reduces to the green Cr³⁺ ion

Aldehydes can also be oxidised Tollen's reagent. This are used as a test for the presence of aldehyde groups

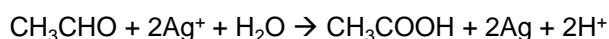
Tollen's Reagent

Reagent: Tollen's reagent formed by mixing aqueous ammonia and silver nitrate. The active substance is the complex ion of [Ag(NH₃)₂]⁺.

Conditions: heat gently

Reaction: **aldehydes only** are oxidised by Tollen's reagent into a carboxylic acid. 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.



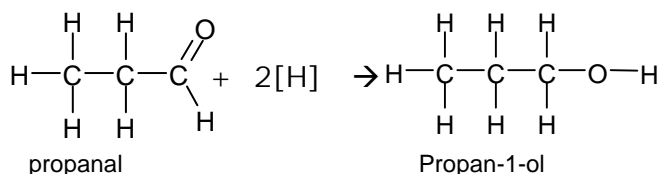
Reduction of carbonyls

Reagents: NaBH₄ in aqueous ethanol

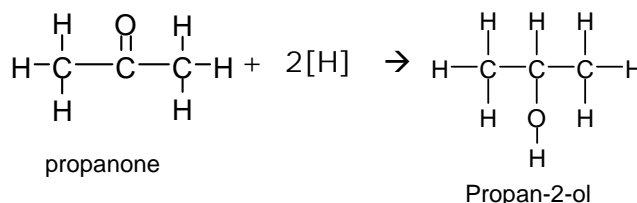
Conditions: Room temperature and pressure

Reducing agents such as NaBH₄ (sodium tetrahydridoborate) or LiAlH₄ (lithium tetrahydridoaluminate) will reduce carbonyls to alcohols.

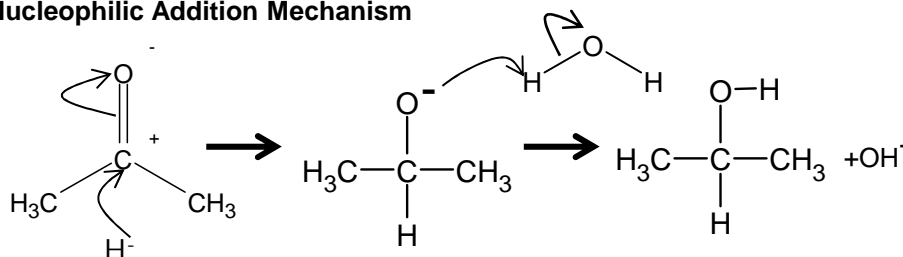
Aldehydes will be reduced to primary alcohols



Ketones will be reduced to secondary alcohols.



Nucleophilic Addition Mechanism



NaBH₄ contains a source of nucleophilic hydride ions (H⁻) which are attracted to the positive carbon in the C=O bond.

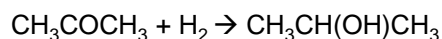
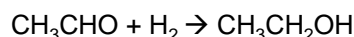
Catalytic Hydrogenation

Carbonyls can also be reduced using catalytic hydrogenation

Reagent: hydrogen and nickel catalyst

Conditions: high pressure

Example Equations



Addition of hydrogen cyanide to carbonyls to form hydroxynitriles

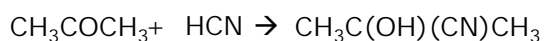
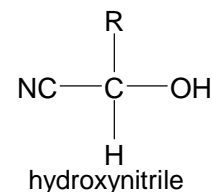
Reaction: carbonyl → hydroxynitrile

Reagent: sodium cyanide (NaCN) and dilute sulfuric acid.

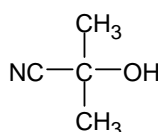
Conditions: Room temperature and pressure

Mechanism: nucleophilic addition

The NaCN supplies the nucleophilic CN⁻ ions. The H₂SO₄ acid supplies H⁺ ions needed in second step of the mechanism



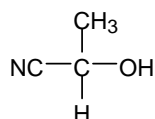
2-hydroxy-2-methylpropanenitrile



When naming hydroxy nitriles the CN becomes part of the main chain

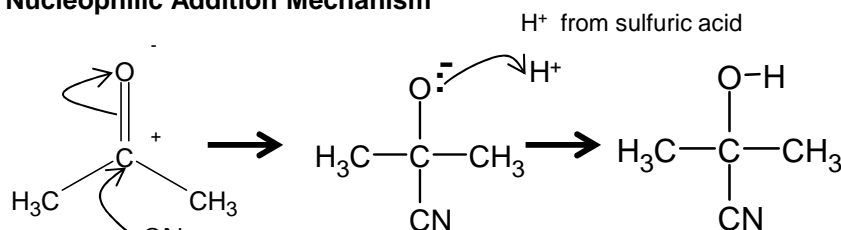


2-hydroxypropanenitrile



We could use HCN for this reaction but it is a toxic gas that is difficult to contain. The KCN/NaCN are still, however, toxic, because of the cyanide ion.

Nucleophilic Addition Mechanism

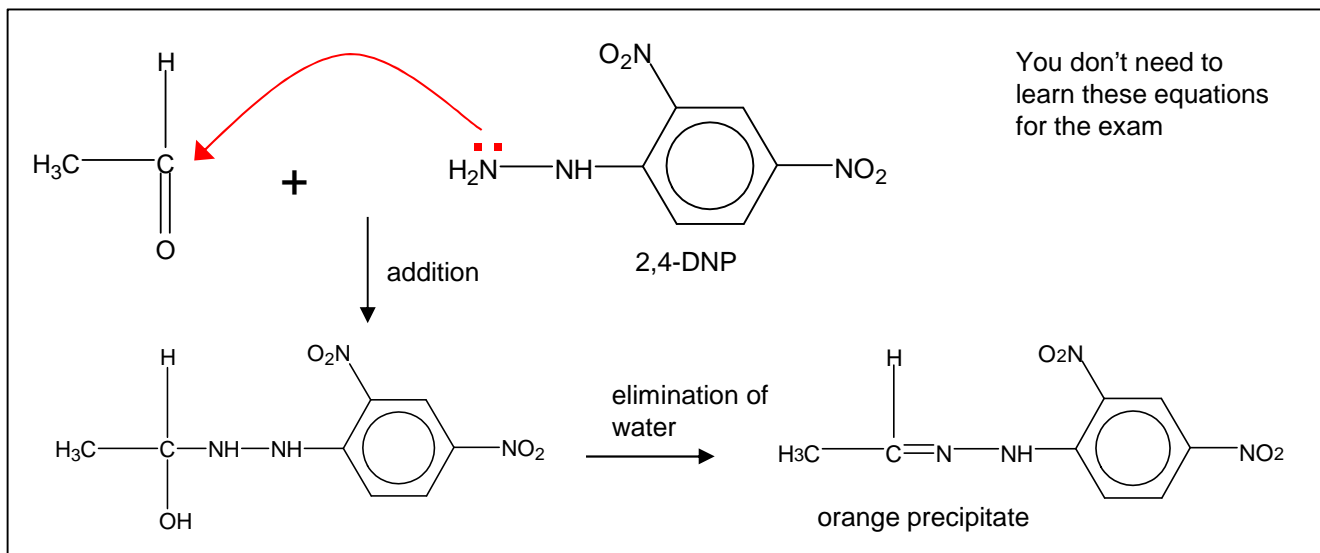


Reaction with 2,4-dinitro phenylhydrazine

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 Tollen's 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



Tollen's Reagent

Reagent: Tollen's 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 Tollen's reagent into a carboxylic acid. 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.

