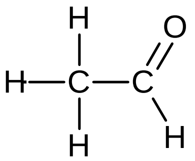
6.1.2 Carbonyl Compounds

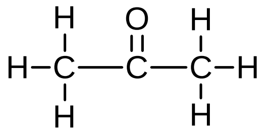
Carbonyls: Aldehydes and Ketones

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**

CH_3CHO ethan**al**

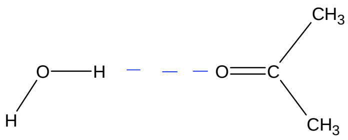


If the C=O is in the middle of the chain it is a ketone
The name will end in **-one**

CH_3COCH_3 propan**one**

Solubility in water

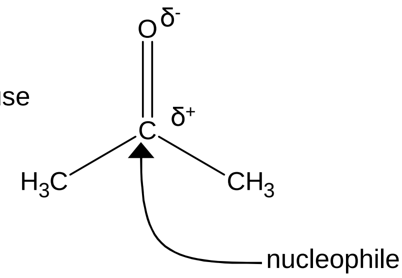
The smaller carbonyls are soluble in water because they can form hydrogen bonds with water.



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

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

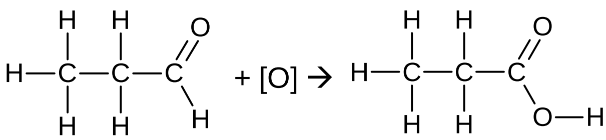
Potassium dichromate $K_2Cr_2O_7$ is an oxidising agent that causes alcohols and aldehydes to oxidise.

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 sulphuric acid.
Conditions: heat under reflux



$RCHO + [O] \rightarrow RCO_2H$

Full Equation for oxidation

$3CH_3CHO + Cr_2O_7^{2-} + 8H^+ \rightarrow 3\,CH_3CO_2H + 4H_2O + 2Cr^{3+}$

Observation: the orange dichromate ion ($Cr_2O_7^{2-}$) reduces to the green Cr^{3+} 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 $[Ag(NH_3)_2]^+$.

Conditions: heat gently

Reaction: aldehydes only are oxidised by Tollen's 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.

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

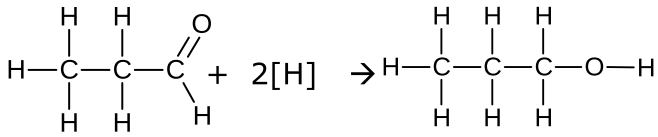
Reduction of carbonyls

Reagents: $NaBH_4$ In aqueous ethanol

Conditions: Room temperature and pressure

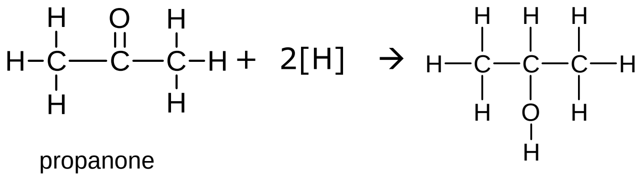
> Reducing agents such as $NaBH_4$ (sodium tetrahydridoborate) or $LiAlH_4$ (lithium tetrahydridoaluminate) will reduce carbonyls to alcohols.

Aldehydes will be reduced to primary alcohols



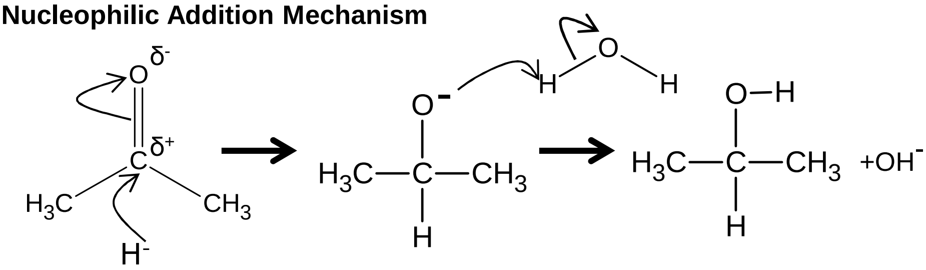
propanal Propan-1-ol

Ketones will be reduced to secondary alcohols.



propanone Propan-2-ol

Nucleophilic Addition Mechanism



> $NaBH_4$ contain 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

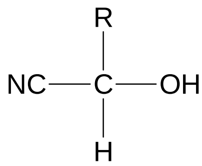
$CH_3CHO + H_2 \rightarrow CH_3CH_2OH$

$CH_3COCH_3 + H_2 \rightarrow CH_3CH(OH)CH_3$

Addition of hydrogen cyanide to carbonyls to form hydroxynitriles

Reaction: carbonyl → hydroxynitrile
Reagent: sodium cyanide (NaCN) and dilute sulphuric acid.
Conditions: Room temperature and pressure
Mechanism: nucleophilic addition

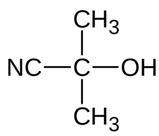
> The NaCN supplies the nucleophilic CN^- ions. The H_2SO_4 acid supplies H^+ ions needed in second step of the mechanism



hydroxynitrile

$CH_3COCH_3 + HCN \rightarrow CH_3C(OH)(CN)CH_3$

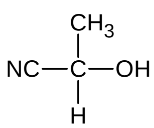
2-hydroxy-2-methylpropanenitrile



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

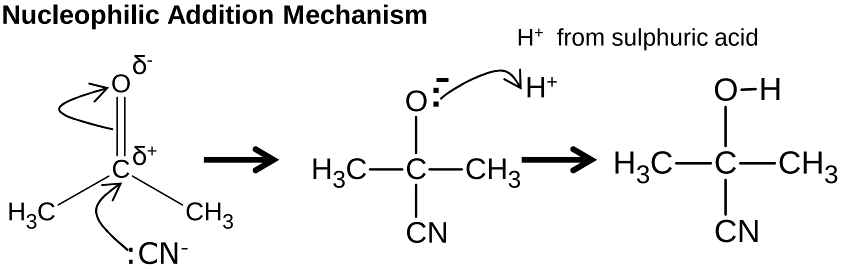
$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$

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



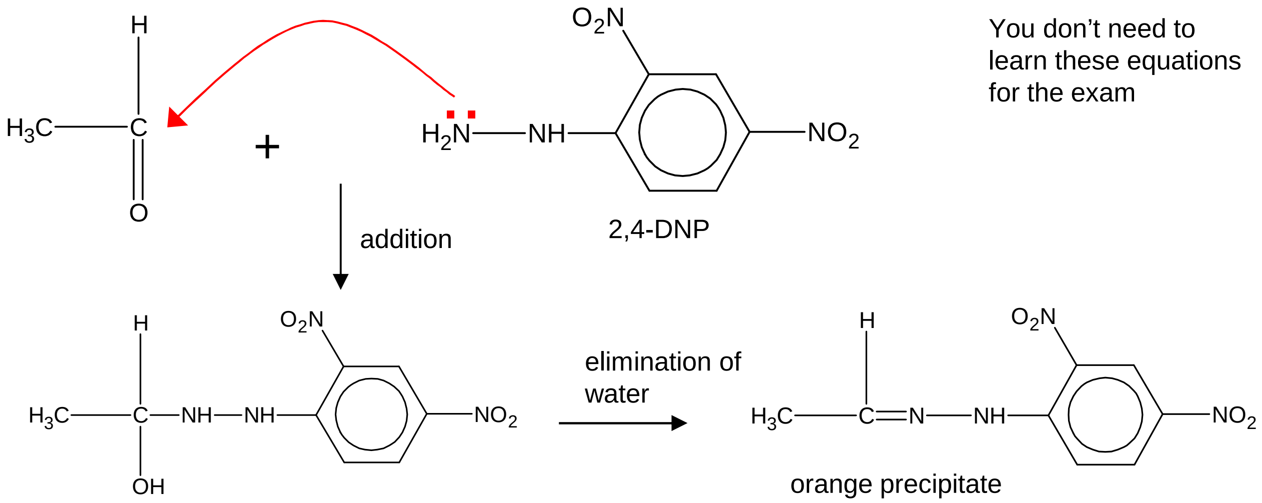
Reaction with 2,4-dinitro phenylhydrazine

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

You don't need to learn these equations for the exam



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