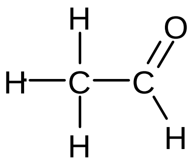
3.8 Aldehydes and Ketones

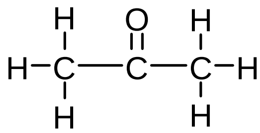
Carbonyls: Aldehydes and Ketones

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



CH_3CHO ethan**al**

If the C=O is on the end of the chain with an H attached it is an <u>aldehyde</u>.
The name will end in **–al**



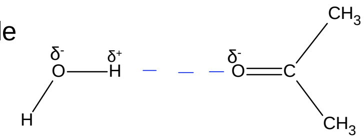
CH_3COCH_3 propan**one**

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

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

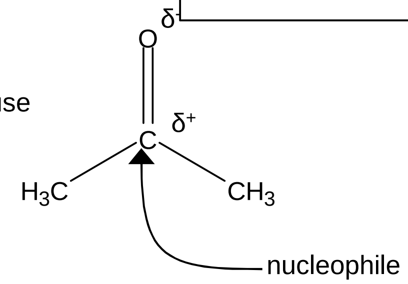
Solubility in water

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



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

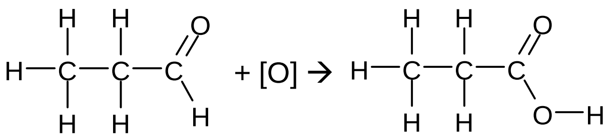
Potassium dichromate $K_2Cr_2O_7$ is an oxidising agent that causes alcohols and aldehydes to oxidise.

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 sulfuric 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 using Fehling's solution or Tollen's reagent. These are used as tests 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. 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.

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

Fehling's solution

Reagent: Fehling's solution containing blue Cu^{2+} ions.
Conditions: heat gently
Reaction: aldehydes only are oxidised by Fehling's Solution into a carboxylic acid. The copper (II) ions are reduced to copper(I) oxide . .
Observation: Aldehydes : Blue Cu^{2+} ions in solution change to a red precipitate of Cu_2O. **Ketones do not react.**

$$CH_3CHO + 2Cu^{2+} + 2H_2O \rightarrow CH_3COOH + Cu_2O + 4H^+$$

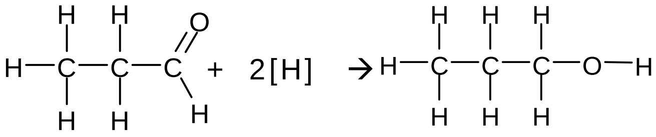
Reduction of carbonyls

Reagents: $NaBH_4$ In aqueous ethanol

Conditions: Room temperature and pressure

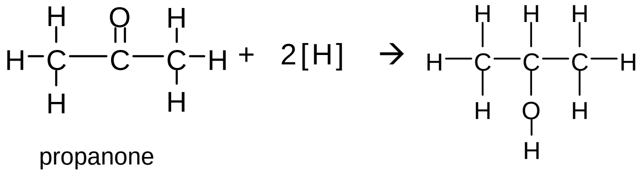
Reducing agents such as $NaBH_4$ (sodium tetrahydridoborate) or $LiAlH_4$ (lithium tetrahydridoaluminate) will reduce carbonyls to alcohols.

Aldehydes will be reduced to primary alcohols



propanal → Propan-1-ol

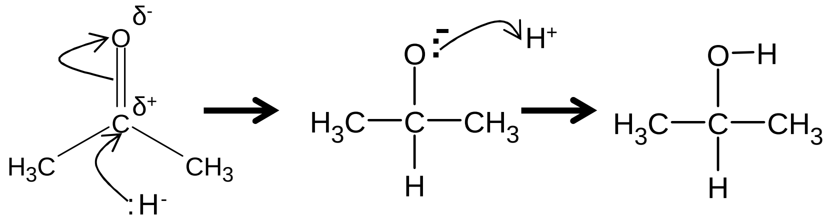
Ketones will be reduced to secondary alcohols.



propanone → Propan-2-ol

Nucleophilic Addition Mechanism

H^+ from water or weak acid



$NaBH_4$ 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

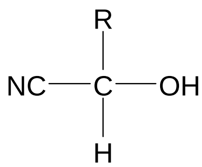
$CH_3CHO + H_2 \rightarrow CH_3CH_2OH$

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

Addition of hydrogen cyanide to carbonyls to form hydroxynitriles

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

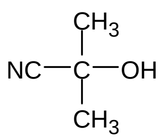
The NaCN supplies the nucleophilic CN^- ions. The H_2SO_4 acid supplies H^+ ions needed in second step of the mechanism



hydroxynitrile

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

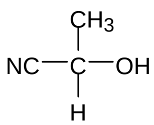
2-hydroxy-2-methylpropanenitrile



When naming hydroxy nitriles the CN becomes part of the main chain and carbon nº 1

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

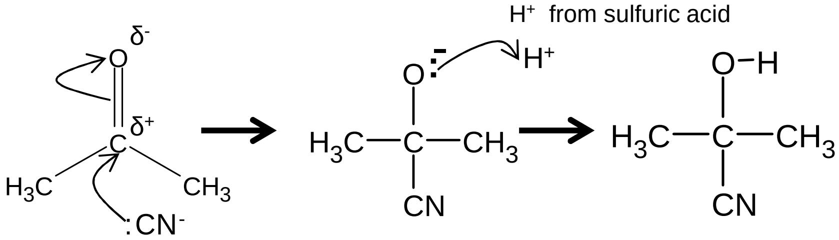
2-hydroxypropanenitrile



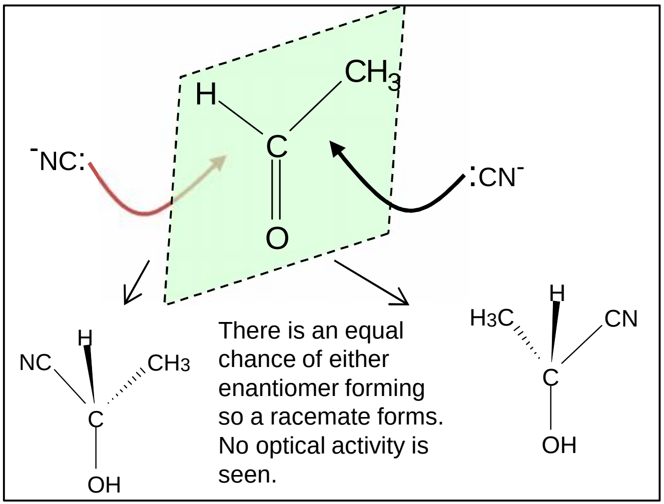
We could use HCN for this reaction but it is a toxic gas that is difficult to contain. KCN/NaCN are still, however, toxic, because of the cyanide ion.

Nucleophilic Addition Mechanism

H^+ from sulfuric acid



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)