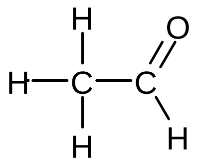
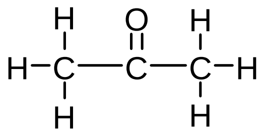
Carbonyls: Aldehydes and Ketones

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**

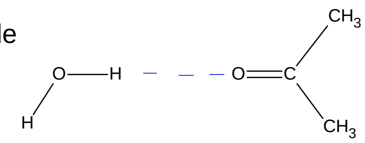


CH_3COCH_3 propan**one**

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

Solubility in water

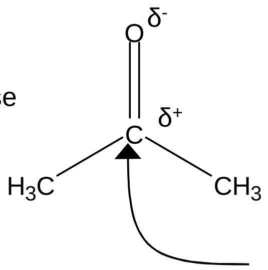
The smaller carbonyls are soluble in water because they can form hydrogen bonds with water.



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

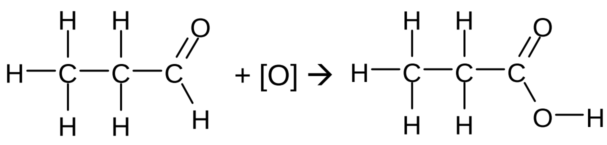
Potassium dichromate $K_2Cr_2O_7$ is an oxidising agent that causes alcohols and aldehydes to oxidise.

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 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

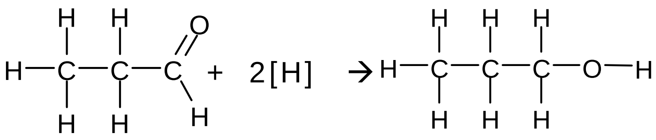
Reduction of carbonyls

Reagents: $NaBH_4$ In aqueous ethanol

Conditions: Room temperature and pressure

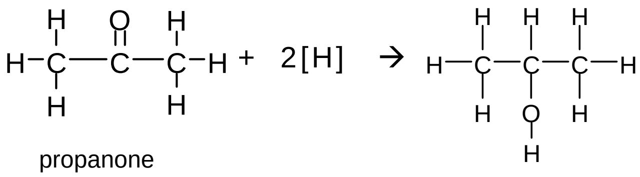
Reducing agents such as $NaBH_4$ (sodium tetrahydridoborate) or $LiAlH_4$ (lithium tetrahydridoaluminate) will reduce carbonyls to alcohols.

Aldehydes will be reduced to primary alcohols



propanal — Propan-1-ol

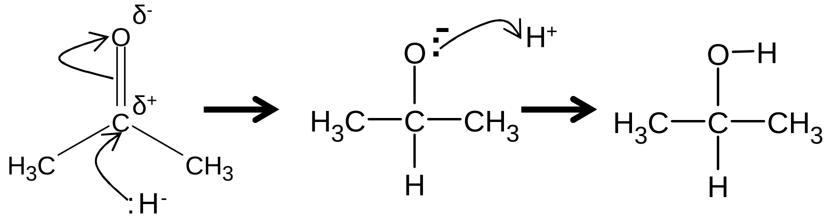
Ketones will be reduced to secondary alcohols.



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

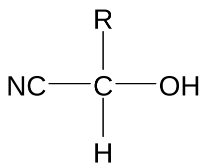
$CH_3CHO + H_2 \rightarrow CH_3CH_2OH$

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

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

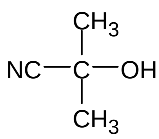
The NaCN supplies the nucleophilic CN^- ions. The H_2SO_4 acid supplies H^+ ions needed in second step of the mechanism



hydroxynitrile

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

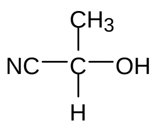
2-hydroxy-2-methylpropanenitrile



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

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

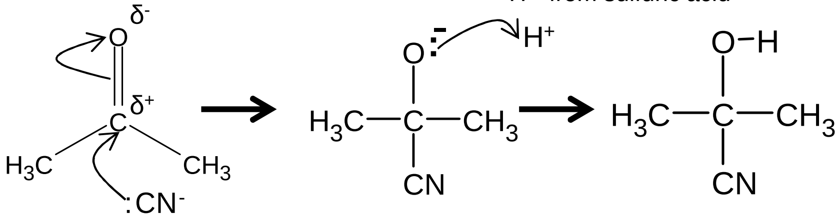
2-hydroxypropanenitrile



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.

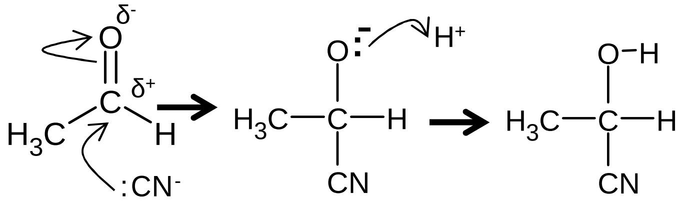
Nucleophilic Addition Mechanism

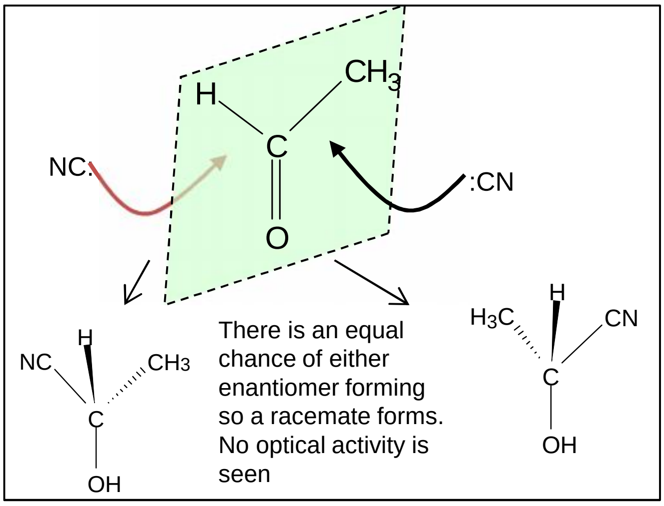
H^+ from sulfuric acid



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)



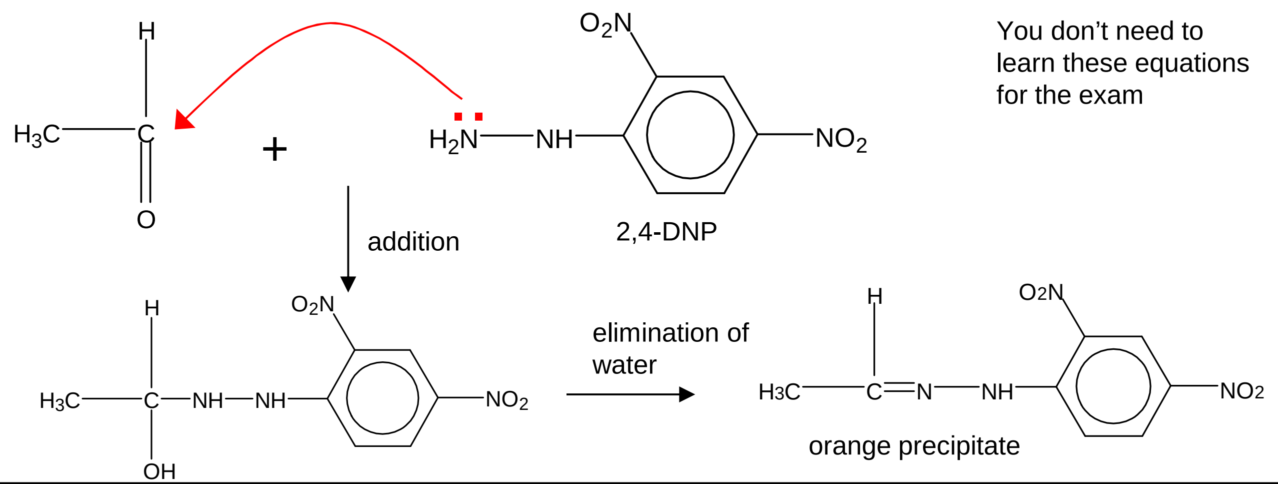


Reaction with 2,4-dinitro phenylhydrazine

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

Functional group tests for an Aldehyde

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.

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

Tollen's reagent method

Place 1 cm^3 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 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 Cu^{2+} ions in solution change to a red precipitate of Cu_2O. **Ketones do not react**

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

Fehling's solution method

Place 1 cm^3 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.

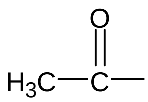
Reaction of carbonyls with iodine in presence of alkali

Reagents: Iodine and sodium hydroxide

Conditions: warm very gently

The product CHI_3 is a yellow crystalline precipitate with an antiseptic smell

Only carbonyls with a methyl group next to the C=O bond will do this reaction. Ethanal is the only aldehyde that reacts. More commonly is methyl ketones.



This reaction is called the Iodoform test

$$CH_3COCH_3 + \mathbf{3}I_2 + \mathbf{4}NaOH \rightarrow CHI_3 + CH_3COONa + \mathbf{3}NaI + \mathbf{3}H_2O$$

$$CH_3COCH_2CH_3 + \mathbf{3}I_2 + \mathbf{4}NaOH \rightarrow CHI_3 + CH_3CH_2COONa + \mathbf{3}NaI + \mathbf{3}H_2O$$