Carbonyls

Aldehydes and Ketones

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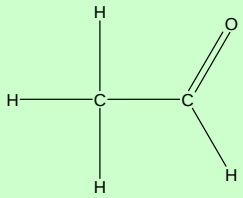
Carbonyls are compounds with a C=O bond, they can be either aldehydes or ketones.

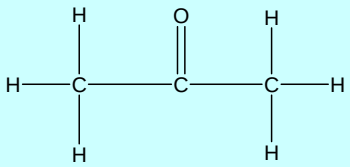


CH_3CHO

ethanal

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



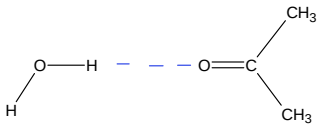
CH_3COCH_3

propanone

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

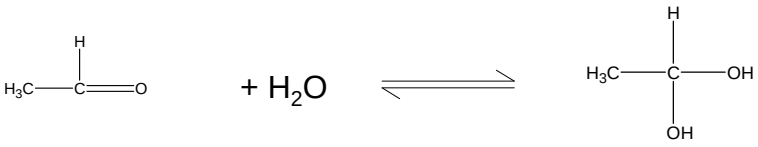
Solubility in water

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 bonding.)

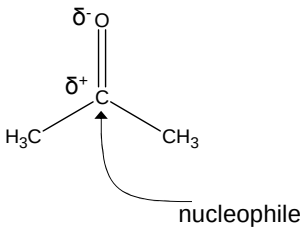
In addition to the hydrogen bonding, water acts as a nucleophile and adds to the double bond.



Reactions of carbonyls

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

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



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

Reaction 1: Oxidation

Revision of module 2

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

Reagents: Sodium dichromate and sulphuric acid

Conditions : heat under reflux

$RCHO + [O] \rightarrow RCO_2H$

Full Equation for oxidation

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

ethanal ethanoic acid

The colour of the reaction mixture changes from orange to green.

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

Test for presence of aldehyde :Fehlings

- **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 ions are reduced to a red precipitate of copper(I) oxide . (**ketones do not react**) .
- Learn the colour change **of Blue Cu $^{2+}$ ions in solution to red precipitate of Cu_2O**

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

Blue solution

red precipitate

Test for presence of 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 coating the inside of the test tube .

The silver coating the inside of test tube is called a silver mirror. (**ketones do not react**)

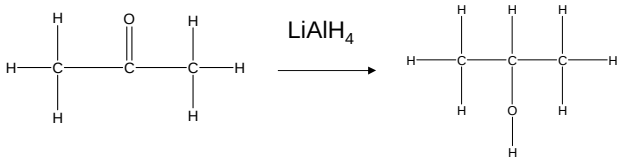
$$CH_3CHO + 2Ag^+ + H_2O \rightarrow CH_3COOH + 2Ag + 2H^+$$

reaction 2: Reduction of carbonyls

Use a reducing agent such as $NaBH_4$ (sodium tetrahydridoborate) or $LiAlH_4$ (lithium tetrahydridoaluminate). These contain nucleophilic hydride ions (H^-) which are attracted to the positive carbon in the C=O bond.

Aldehydes will be reduced to primary alcohols

Ketones will be reduced to secondary alcohols.



propanone

Propan-2-ol

$LiAlH_4$ must be used in anhydrous conditions

Reduction of carbonyls using $NaBH_4$

Change in Functional Group: Carbonyl to alcohol

Reagents $NaBH_4$ (In aqueous ethanol)

Conditions Room temperature

Equations using [H]

Aldehyde → Primary alcohol

$CH_3CHO + 2[H] \longrightarrow CH_3CH_2OH$ primary alcohol

Ketone → Secondary alcohol

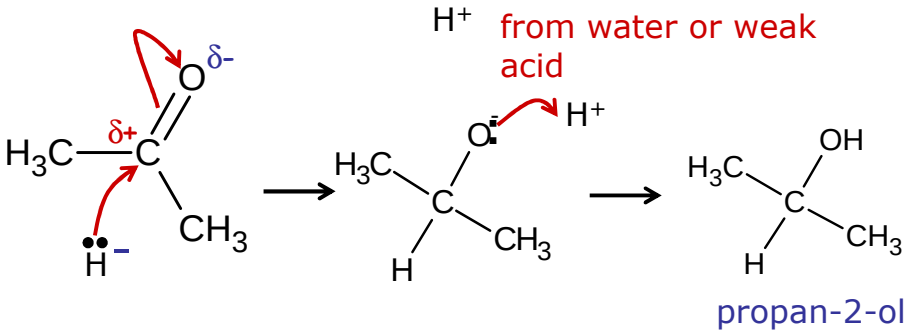
$CH_3COCH_3 + 2[H] \longrightarrow CH_3CH(OH)CH_3$ secondary alcohol

Mechanism for reduction: Nucleophilic Addition

Nucleophilic Addition Mechanism

reduction of propanone

$NaBH_4$ is a source of **hydride ions** H^-



Catalytic Hydrogenation

Carbonyls can also be reduced using catalytic hydrogenation

Reagent: hydrogen and nickel catalyst

Conditions: high pressure

Example Equations

$CH_3CHO + H_2 \rightarrow CH_3CH_2OH$

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

Reaction 3 :Addition of hydrogen cyanide to carbonyls to form hydroxynitriles

Change in Functional Group: Carbonyl to hydroxynitrile

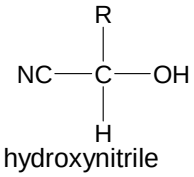
Reagents NaCN (aq) and H_2SO_4(aq) supplies H^+
supplies the CN^- nucleophile

Conditions Room temperature

Equations

$RCOR + HCN \longrightarrow RC(OH)(CN)R$

$RCHO + HCN \longrightarrow RCH(OH)CN$



hydroxynitrile

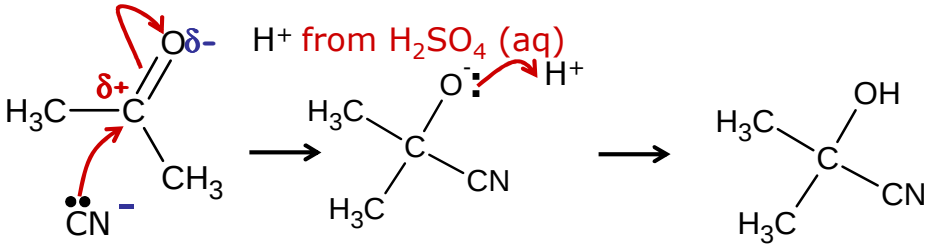
Mechanism: Nucleophilic Addition

Nucleophilic Addition Mechanism

hydrogen cyanide with propanone

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

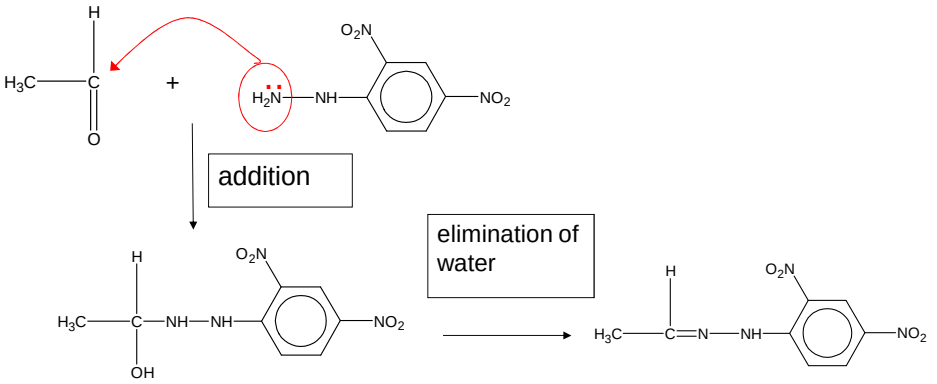
NaCN (aq) is a source of **cyanide ions** $:C\equiv N^-$



2-hydroxy-2-methylpropanenitrile

Reaction : Brady's reagent

Brady's reagent is 2,4-dinitro phenylhydrazine also known as 2,4-d.n.p. It contains a nucleophilic nitrogen (that has a lone pair of electrons) that is attracted to the positive carbon.



Extra

Identifying Carbonyls with Brady's Reagent

The product is an orange red crystal, this reaction occurs with both aldehydes and ketones. It can be used as a test for a carbonyl group.

Use brady's reagent to identify if the compound is a carbonyl, then to differentiate an aldehyde from a ketone use benedict's solution.

The melting point of the crystal formed can be used to help identify which carbonyl was used.

Extra