4.4 - Aldehydes and ketones

Formation

Aldehydes and ketones are formed by the oxidation of primary and secondary alcohols respectively with acidified dichromate ($Cr_2O_7^{2-}$ / H^+).

The formation of the aldehyde requires gentle warming. The aldehyde is distilled off as it forms to prevent complete oxidation to the carboxylic acid. This is not required for the ketone, as the ketone cannot be oxidised any further.

Primary

$RCH_2OH \rightarrow RCHO \rightarrow RCOOH$

aldehyde carboxylic acid

Secondary

ketone

Distinguishing between aldehydes and ketones

Aldehydes and ketones may be distinguished from each other as aldehydes can be oxidised, whereas ketones cannot.

Two common reagents used to distinguish between an aldehyde and a ketone are Fehling's solutions and Tollens' reagent.

Tollens' reagent is ammoniacal silver nitrate which produces a silver mirror if an aldehyde is present. Silver ions oxidise the aldehyde and are themselves reduced to silver atoms.

$Ag^+ + e^- \rightarrow Ag$

colourless silver mirror

There is no change with a ketone.

Fehling's solution is a Cu^{2+} complex which turns from blue to red when an aldehyde is present. Cu^{2+} ions oxidise the aldehyde and are themselves reduced to Cu^+ ions.

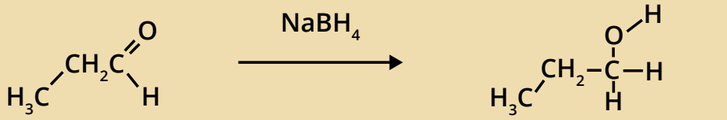
$Cu^{2+} + e^- \rightarrow Cu^+$

blue red

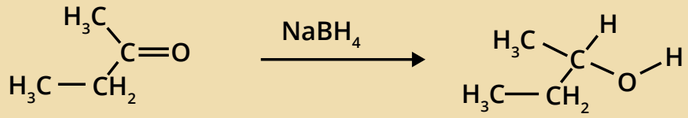
Again there is no change with a ketone.

Reduction

Aldehydes and ketones (carbonyl group) can be reduced using sodium tetrahydridoborate(III), $NaBH_4$, in aqueous solution. The aldehyde reduces to a primary alcohol and the ketone to a secondary alcohol.



propanal propan-1-ol
a primary alcohol

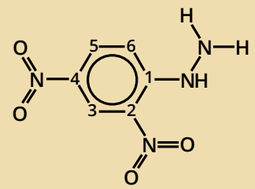


butan-2-ol
a secondary alcohol

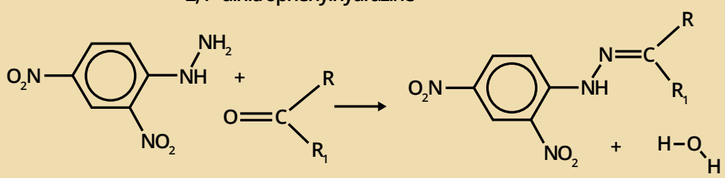
Identifying aldehydes and ketones

2,4-DNP (2,4-dinitrophenylhydrazine) can be used to test for an aldehyde or ketone. The reaction which takes place is an addition-elimination or condensation reaction.

When a carbonyl compound reacts with 2,4-DNP, a yellow or orange solid forms. This solid can be isolated and purified and the original aldehyde or ketone identified from its melting temperature.



2,4-dinitrophenylhydrazine

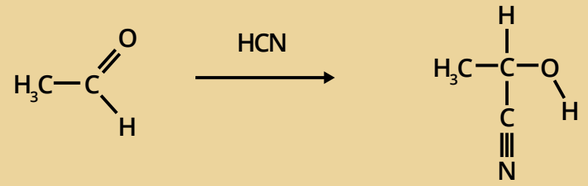


The product is called a 2,4-dinitrophenylhydrazone.

Nucleophilic addition of HCN

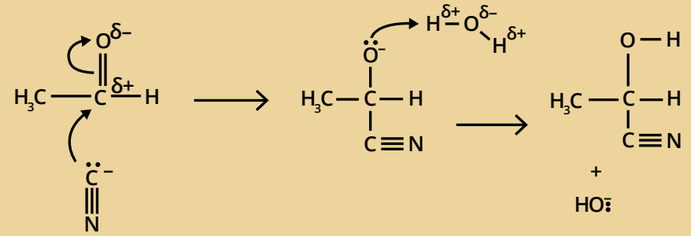
Carbonyl compounds will undergo a nucleophilic addition reaction with hydrogen cyanide, HCN. The rate is slow but is greatly increased by addition of alkali or cyanide ions.

e.g. $CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$



2-hydroxypropanenitrile

The mechanism for this nucleophilic addition reaction is as follows.



Nucleophilic attack by cyanide ion at the carbon atom of the polar carbonyl group

The resulting negative ion gains a proton from water (solvent) or any other available molecule such as HCN

Iodoform reaction

This is a reaction which is used to identify a carbonyl compound that contains CH_3CO— (ethanal and methyl ketones) and alcohols that contain CH_3CHOH— (ethanol and methyl secondary alcohols).

The reagents required are either iodine and aqueous sodium hydroxide **or** aqueous potassium iodide and aqueous sodium chlorate(I), NaClO.

A positive result will produce a yellow precipitate of triiodomethane, CHI_3, which has a characteristic antiseptic smell.