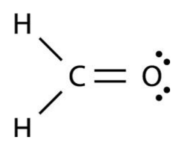
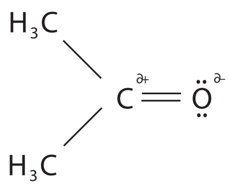
Year 2, Organic Chemistry, Chapter 20: The Reactions of Ketones

- A Carbonyl compound has the form " **RR' >C=O** ", and the difference between a Ketone and an Aldehyde is that in a Ketone each "R" species represents an alkyl group. If one of the "R" species were an "H" species, then the compound would be an Aldehyde. By definition therefore if both of the "R" species is an "H" then the compound would certainly be an Aldehyde – in fact it would be Methanal (it would have only one C atom, therefore it would be a "meth–" species).

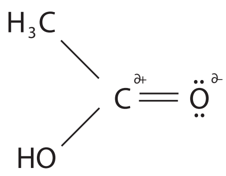


- If one of the "R" species in " **RR' >C=O** " were an hydroxy species ("–OH") then the compound would be a Carboxylic Acid, and if instead of it being an "–OH" species the "R" species were a "Cl" species, then it would be an Acyl Chloride.

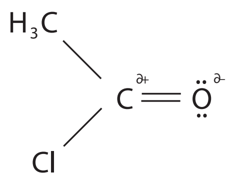
- A Ketone has the structure on the left below, and the one below is the simplest Ketone that there is. It is called propan-2-one, and its common name is acetone. The names of all Ketones end in "–one".



Propan-2-one



Ethanoic Acid



Ethanoyl Chloride

- The structure on the left above has three C atoms therefore it must a "prop–" Ketone. The structure in the middle has only two C atoms therefore it must be an "eth–" acid, and the acyl chloride on the right also has two C atoms therefore it must be "ethanoyl" acyl chloride.

- I trust that you now have a clear idea of what constitutes a Ketone. The name must end in "–one", and the location of the ">C=O" group must be stated quite clearly.

- As is the case with an Aldehyde, it is possible to get from a Ketone to an acid via a Nitrile, but please remember that if you go through a Nitrile then you will be increasing the length of the Carbon chain by one C atom.

- **HCN is very toxic. Instead use NaCN or KCN and some dilute H_2SO_4.**

ALDEHYDE

O
||
R – C – **H**

KETONE

O
||
R – C – **R1**

Ketones resist gentle oxidisation.

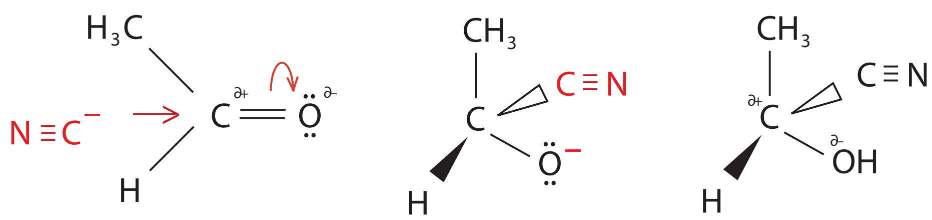
Under gentle oxidisation with $K_2Cr_2O_7$ and conc H_2SO_4, Aldehydes are converted into Carboxylic Acids.

$LiAlH_4$ will reduce an Aldehyde to a 1˚ Alcohol, and a Ketone into a 2˚ alcohol.

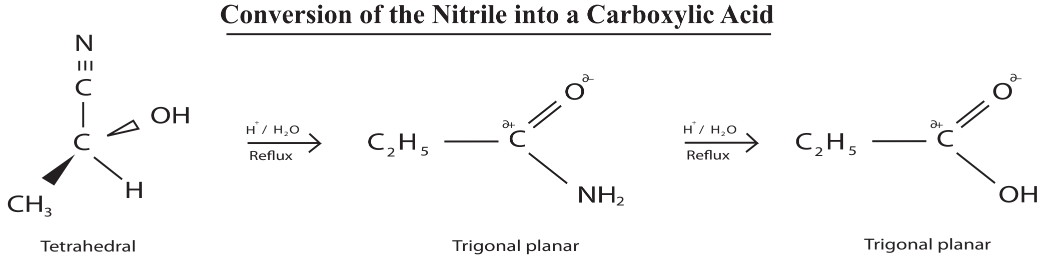
Test for an Aldehyde
It will react with Tollens (silver ppt),
and with Fehling's or Benedict's
(cyan Cu2+ goes reddy-brown because of Cu+ ppt).

Test for a Ketone
It will ***not*** react with Tollens (silver ppt),
nor with Fehling's nor Benedict's
because Ketones resist gentle oxidisation.

Both Aldehydes and Ketones undergo Nucleophilic attack on the C atom that has been denuded of electron density by the highly electronegative O atom. If the attacking Nucleophile is a Cyanate ("CN") species then a Nitrile is formed.



Conversion of the Nitrile into a Carboxylic Acid



The reactions of Ketones

A) **Brady's reagent** will turn all Carbonyl compounds into an orangey/yellow colour[1] and thus it will do so with a Ketone – and most (but not all) Ketones will respond to the Iodoform test and produce the fine yellow crystals of CHI_3.

B) Ketones resist gentle oxidisation therefore they **are not oxidise**d to Carboxylic Acids by acidified Potassium Dichromate and will not respond to the **Tollen's**/**Fehling's**/or **Benedict's** tests.

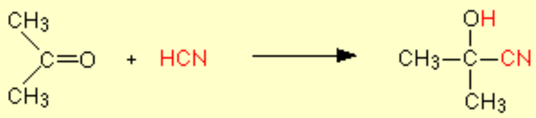
[1] Brady's reagent cannot distinguish between an Aldehyde and a Ketone, but the Iodoform test can **(a Ketone will produce a precipitate of yellow crystals).**

D) The action of the **Reduction**[2] **of a Ketone to a 2° Alcohol** using Sodium-tetrahydrido-borate ($NaBH_4$) or else Lithium-tetrahydrido-aluminate ($LiAlH_4$) is similar to that of an Aldehyde (cf. Chapter 19).

E) The **Nucleophilic Addition** reaction with Hydrogen Cyanide (HCN) to create a Nitrile is similar to that for an Aldehyde (cf. Chapter 19).

- Jim Clark says the following.

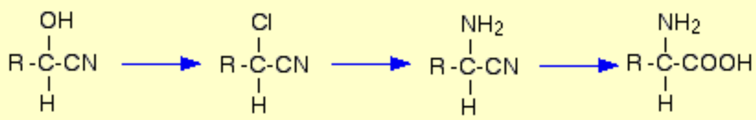
With propanone (a ketone) you get 2-hydroxy-2-methylpropanenitrile:



The product molecules contain two functional groups:

- the -OH group which behaves like a simple alcohol and can be replaced by other things like chlorine, which can in turn be replaced to give, for example, an $-NH_2$ group;
- the -CN group which is easily converted into a carboxylic acid group -COOH.

For example, starting from a hydroxynitrile made from an aldehyde, you can quite easily produce relatively complicated molecules like 2-amino acids - the amino acids which are used to construct proteins.



- I have put the following table here as a reminder of some of the reactions involved.

[2] Reduction can be defined in terms of OILRIG, or it can be described in terms of the loss of Oxygen atoms from a species or the gain of Hydrogen atoms by that species.

ALDEHYDES and KETONES

- Tertiary Alcohols do not oxidise readily unless you use very aggressive oxidising agents that break Carbon–Carbon bonds

- Test for Aldehydes and Ketones
Brady's reagent is 2,4-DNPH, [H2N–NH(C6H3(NO2)2], mixed with Methanol and Sulphuric Acid,
and when an Aldehyde or a Ketone comes into contact with Brady's Reagent
then a reddy/ orangey/yellow precipitate is formed. (2,4-DNPHydrazine becomes 2,4-DNP Hydrazone.)

1° **Alcohol** + K2Cr2O7 and conc H2SO4
or **Nitrile** plus HCl plus water
or **Acyl Chloride** plus Water
or **Acid Anhydride** plus Water (Reflux)
or **Amide** with H^+ and Water

→ **CARBOXYLIC ACIDS**

Hydrolyse with H2SO4

AMIDE

+ HCl at 140˚C

NITRILE

Oxidise with K2Cr2O7 and conc H2SO4

+ HCN is toxic, so use NaCN and a bit of conc H2SO4

Test for an Aldehyde
It will react with Tollens (silver ppt),
and with Fehling's or Benedict's
(cyan Cu2+ goes reddy-bronwn because of Cu+ ppt).

ALDEHYDES

Oxidise with K2Cr2O7 and conc H2SO4

Reduce with LiAlH4 or NaBH4

- ESTER
Reflux with a Carboxylic Acid and conc H2SO4

- ETHER
Reflux with conc H2SO4 < 140˚C

Primary
ALCOHOLS
Secondary

- HALOGENOALKANES
Reflux with appropriate Sodium Halide
and conc H2SO4

- ALKENES
Reflux with conc H2SO4 > 170˚C

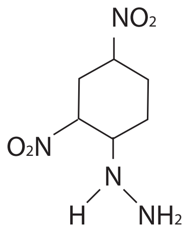
KETONES

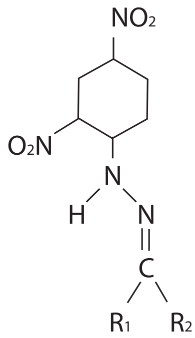
Test for a Ketone
It will not react with Tollens (silver ppt),
nor with Fehling's or Benedict's
(cyan Cu2+ goes reddy-bronwn because of Cu+ ppt).

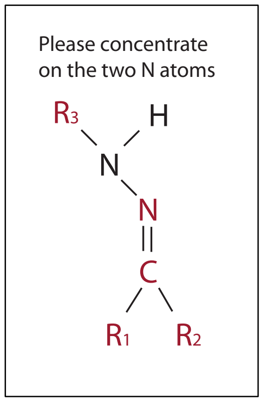
- I think that that is more than enough for 'A' Level purposes.

- The 2,4-DNPH mentioned above is shown overleaf.

2,4-DiNitroPhenylHydrazIne **2,4-DiNitroPhenylHydrazOne**

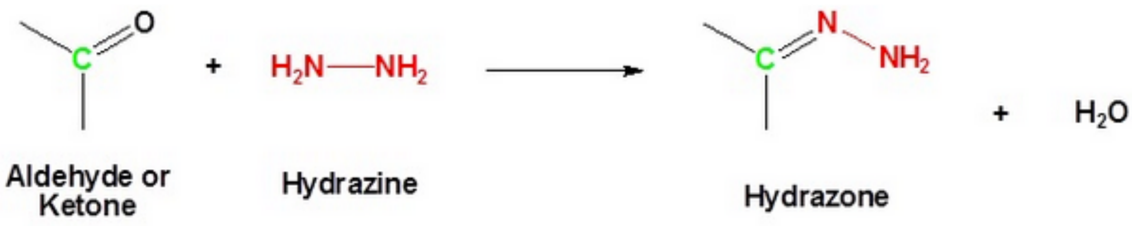






- The only difference between the "**–zine**" and the "**–zone**" is that "zine" has two H atoms attached to the bottom N atom on the right, whilst the "zone" has R_1 and R_2 attached to a C atom which is double bonded to the N atom. ("R" can be any legitimate species, but it is usually an H atom/an alkyl species/or an arene species).

- Writing out the reaction of an Aldehyde or Ketone with the Hydrazine can be daunting for some students, and they find it easier to draw the reaction as follows



Source: Chemistry LibreTexts