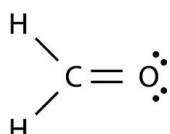
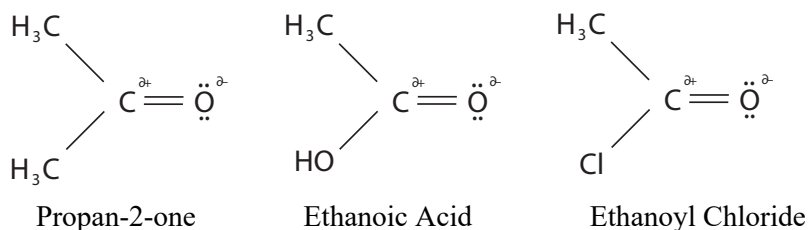


A Second Year Blog on Ketones (for the week commencing the 29th of December 2019)

- A Carbonyl compound has the form “ $\text{RR}'>\text{C}=\text{O}$ ”, 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).

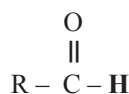


- If one of the “R” species in “ $\text{RR}'>\text{C}=\text{O}$ ” were an hydroxy species (“–OH”) then the compound would be a Carboxylic Acid, and if instead of it being an “–OH” species the “R” species were a “Cl” species, then it would be an Acyl Chloride.
- A Ketone has the structure on the left 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”.

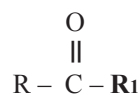


- The structure on the left above has three C atoms therefore it must be a “prop–” Ketone. The structure in the middle has only two C atoms therefore it must be an “eth–” acid, and the acyl chloride on the right also has two C atoms therefore it must be “ethanoyl” acyl chloride.
- I trust that you now have a clear idea of what constitutes a Ketone. The name must end in “–one”, and the location of the “ $>\text{C}=\text{O}$ ” 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 H₂SO₄.**

ALDEHYDE



KETONE



Ketones resist gentle oxidation.

Under gentle oxidation with $\text{K}_2\text{Cr}_2\text{O}_7$ 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.

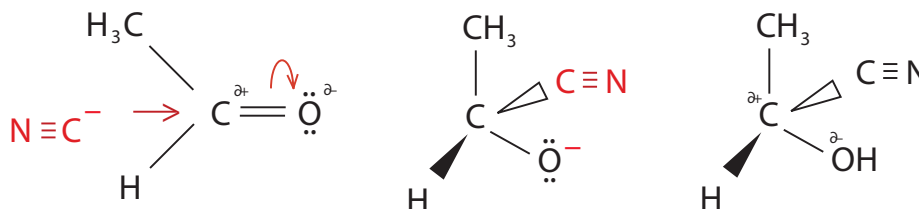
Test for an Aldehyde

It will react with Tollens (silver ppt), and with Fehling's or Benedict's (cyan Cu^{2+} goes reddy-brown because of Cu^+ ppt).

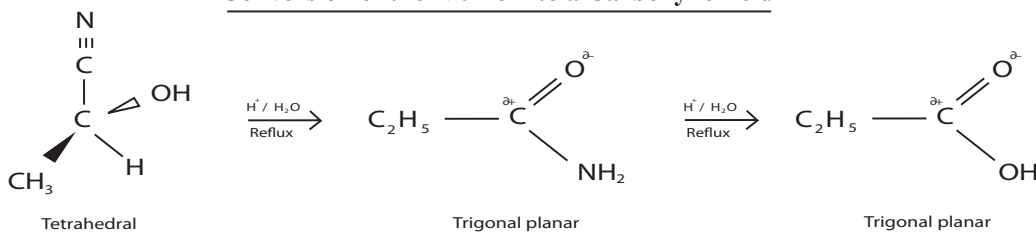
Test for a Ketone

It will *not* react with Tollens (silver ppt), nor with Fehling's nor Benedict's because Ketones resist gentle oxidation.

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 orange/yellow colour¹ 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 oxidation therefore they **are not oxidised** to Carboxylic Acids by acidified Potassium Dichromate and will not respond to the **Tollen's/Fehling's/or Benedict's** tests.

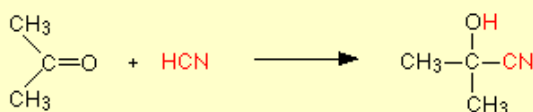
¹ Brady's reagent cannot distinguish between an Aldehyde and a Ketone, but the Iodoform test can (**a Ketone will produce a precipitate of yellow crystals**).

D) The action of the **Reduction² of a Ketone to a 2° Alcohol** using Sodium-tetrahydrido-borate (NaBH₄) or else Lithium-tetrahydrido-aluminate (LiAlH₄) 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.

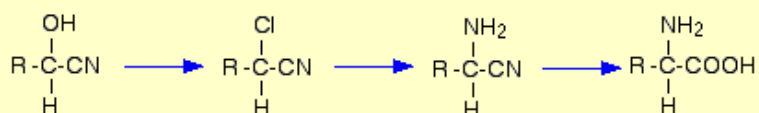
With propanone (a ketone) you get 2-hydroxy-2-methylpropanenitrile:



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 -NH₂ 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.

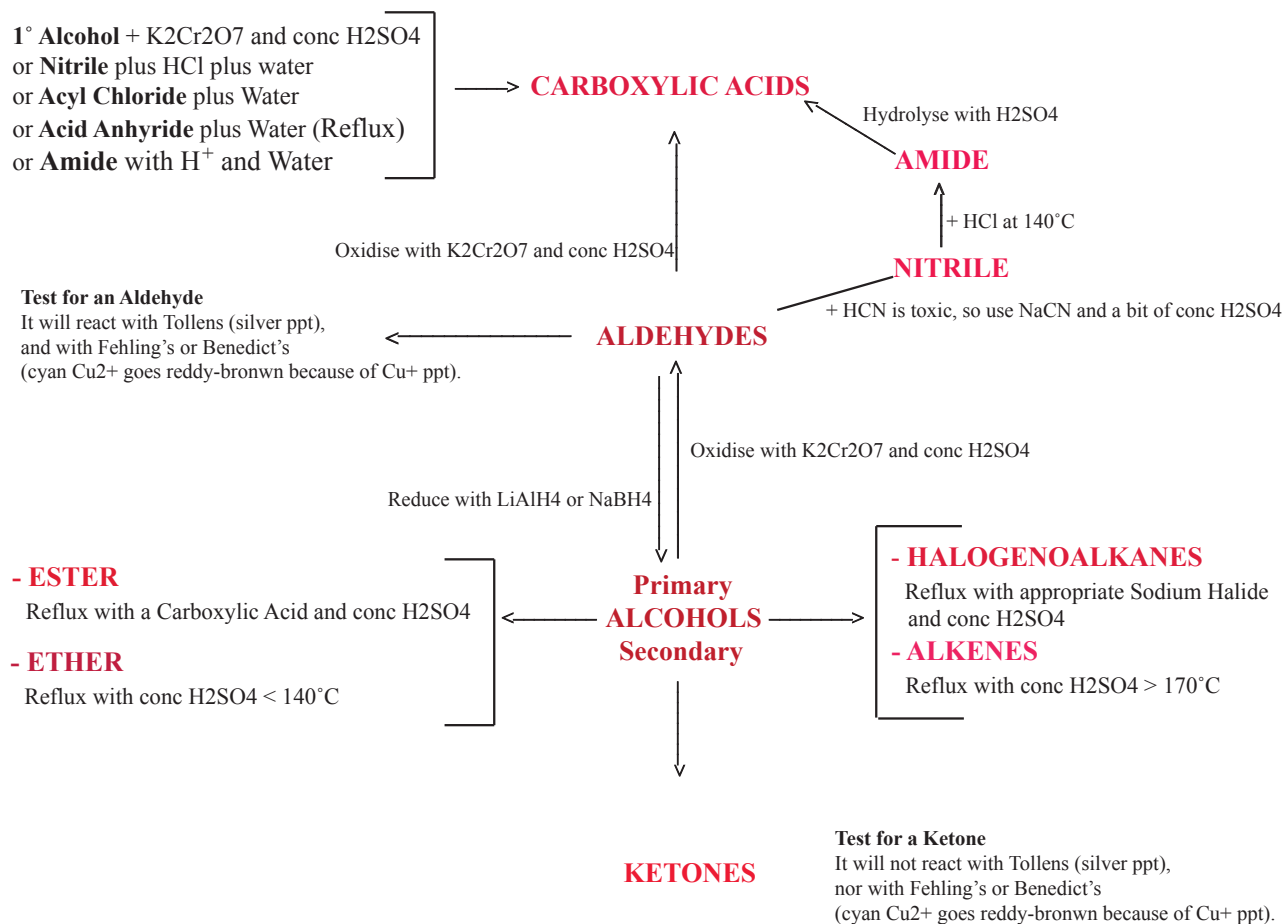
² Reduction can be defined in terms of OILRIG, or it can be described in terms of the loss of Oxygen atoms from a species or the gain of Hydrogen atoms by that species.

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, $[H_2N-NH(C_6H_3(NO_2)_2)]$, 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.)

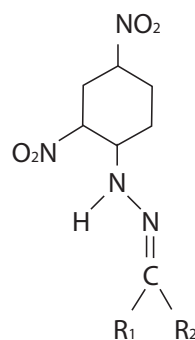
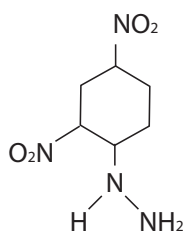


- I think that that is more than enough for 'A' Level purposes.

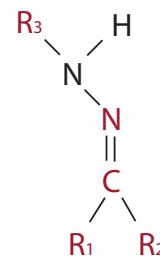
- The 2,4-DNPH mentioned above is shown overleaf.

2,4-DiNitroPhenylHydrazIne

2,4-DiNitroPhenylHydrazOne



Please concentrate
on the two N atoms



- 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 R₁ and R₂ 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).