

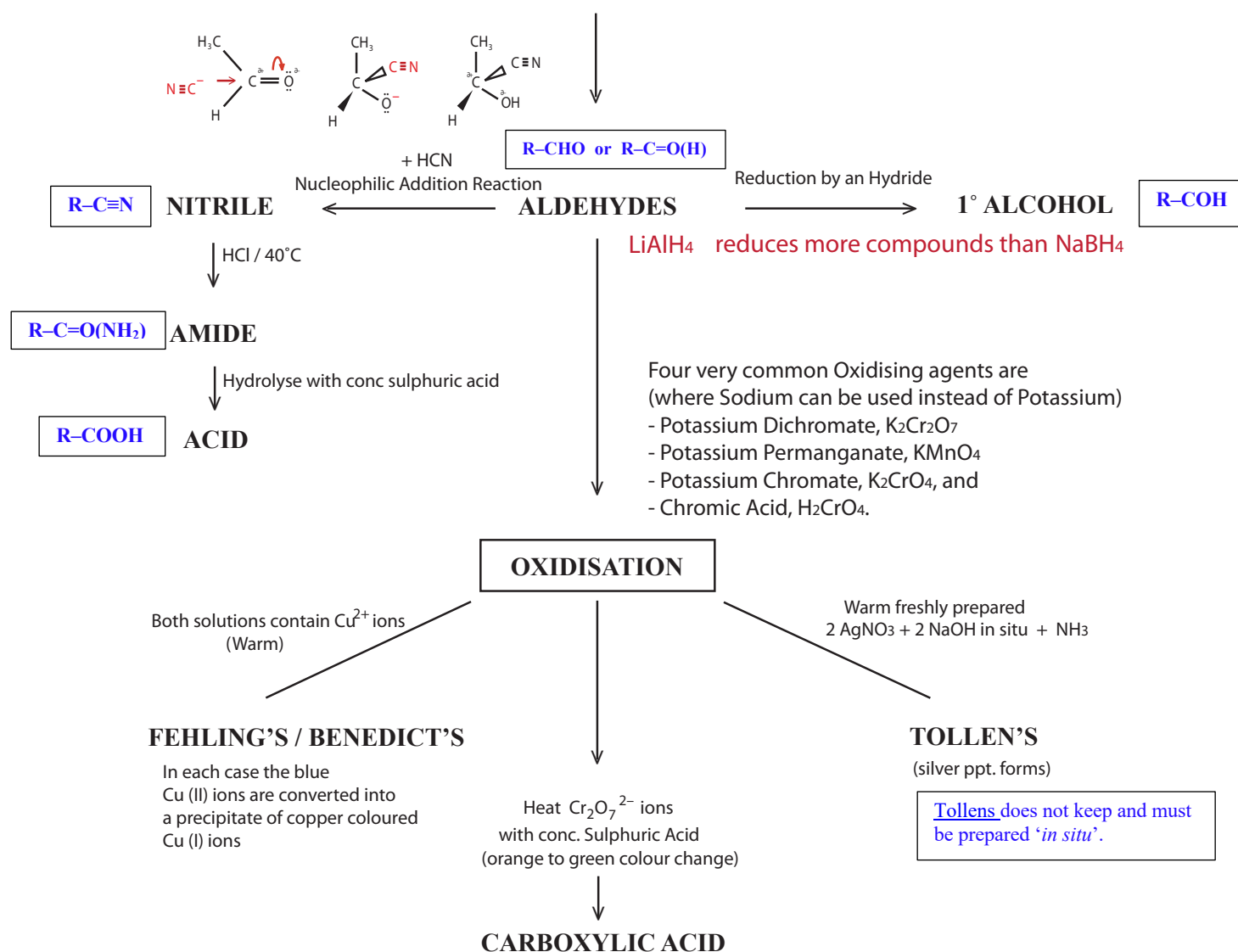
Year 2, Organic Chemistry, Chapter 19:

The Reactions of Aldehydes

Two common routes into Aldehydes

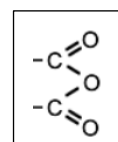
- Oxidisation of a 1° Alcohol (with a dichromate ion/conc sulphuric acid/warm)

- Reduction of an ester, acyl chloride or nitrile to form aldehydes



Please remember that Amines have the form $\text{NR}_1\text{R}_2\text{R}_3$, Nitriles have the form $\text{R}-\text{C}\equiv\text{N}$, Amides have the form

$\text{R}-\text{C}=\text{O}(\text{NH}_2)$, Acyl Chlorides have the form $\text{R}-\text{C}=\text{O}(\text{Cl})$, and Acid Anhydrides have the form



- The following are the main Aldehyde reactions that you need at 'A' Level.

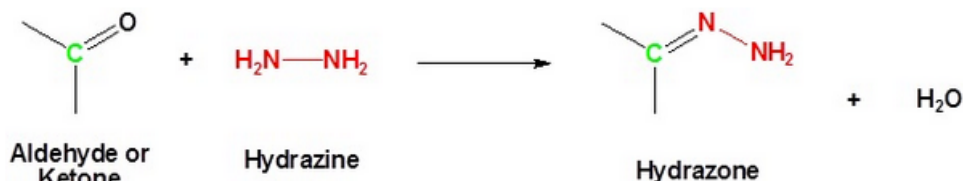
The Oxidisation of Aldehydes into Carboxylic Acids

- With acidified **Potassium Dichromate and concentrated Sulphuric Acid** (just warm the mixture).
- With Tollen's reagent:** warm freshly prepared AgNO_3 and NaOH *in situ* with a small amount of Ammonia and, generally speaking, a silver precipitate will form with an Aldehyde but not with a Ketone (because Aldehydes oxidise and Ketones do not). *However, you need to be aware that all Aldehydes react with Tollen's, but not all the species that react with Tollen's are Aldehydes.*
- Fehling's/Benedict's reagents** (the blue Cu^{2+} complexed ions in the solution are converted into Cu^{1+} ions and the solution turns colourless as the coppery/reddy-brown Cu^{1+} ions are precipitated).

Other Reactions of Aldehydes

- The **reduction of an Aldehyde** to a 1° Alcohol by LiAlH_4 or NaBH_4 (**use LiAlH_4**).
- Reaction with **Brady's reagent** [2,4-DNPH, $[\text{H}_2\text{N}-\text{NH}(\text{C}_6\text{H}_3(\text{NO}_2)_2)]$. Brady's reagent is 2,4-DNPH 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. The Reaction Equation is

$$\text{RR}'\text{C}=\text{O} + \text{H}_2\text{N}-\text{NH}(\text{C}_6\text{H}_3(\text{NO}_2)_2) \rightarrow \text{H}[\text{C}_6\text{H}_3(\text{NO}_2)_2]\text{N}=\text{N}=\text{CRR}' + \text{H}_2\text{O}$$
 where the 2,4-DiNitroPhenylHydrazine becomes 2,4-DiNitroPhenylHydrazone.



Source: Chemistry LibreTexts

(I will talk about Brady's Reagent in greater detail very shortly.)

- The **Iodoform reaction** with Iodine and Sodium Hydroxide to form RCOOH and yellow CHI_3 .
- With **HCN or acidified NaCN** to form first a Nitrile and then an Amide and then an Acid.

NB HCN is dangerous. Use a solution of Sodium Cyanide NaCN (or Potassium Cyanide) to which a little Sulphuric Acid has been added. Mind you, Cyanides also are toxic. (Almost everything in a Chemistry lab is dangerous and should be treated with extreme caution.)

- Aldehydes tend to be more reactive than Ketones, and under **gentle** oxidisation **Aldehydes are oxidised into Carboxylic Acids** (whereas Ketones are not); and, in general, even though they have a double bond, Carbonyl compounds tend **not** to behave like Alkenes and therefore **tend not to undergo electrophilic addition reactions** but instead they are subject to **NUCLEOPHILIC addition** reactions.
- There are variations in the Chemistry 'A' Level Syllabuses for different UK examining boards. The minimum that most exam boards require you to know is as follows (and I shall look at each one of the reactions in turn).

- A) The **ability to test for the presence of an Aldehyde using Brady's reagent** to test for a Carbonyl compound and a recognition of the colour change involved (the appearance of orange/yellow precipitate)¹, followed by the Iodoform test to distinguish between an Aldehyde and a Ketone.
- B) The **ability to test for the presence of an Aldehyde using either Tollen's reagent/Fehling's solution/or Benedict's solution** – with a knowledge of the accompanying colour changes that are involved (the appearance of a silvery grey precipitate for Tollen's, and where the blue solution of Fehling's and Benedict's turns coppery/brown-red, and over a period of time the Copper Oxide precipitate settles to the bottom of the test-tube to leave a colourless solution).
- C) The **Oxidisation of an Aldehyde** to the relevant Carboxylic Acid using acidified Potassium/or Sodium Dichromate together with a knowledge of the relevant colour change (*orange to green*).
- D) The **Reduction² of an Aldehyde to a 1° Alcohol** using Lithium-tetrahydrido-aluminate (LiAlH₄) or else Sodium-tetrahydrido-borate (NaBH₄).
- E) The **Nucleophilic Addition** reaction with Hydrogen Cyanide (HCN) to create a Nitrile – and for Organic Synthesis it is sensible to know that Nitriles can be reacted (with *dilute* Hydrochloric acid) to form the appropriate Carboxylic Acid.

A) Brady's reagent and the Iodoform test (Brady's first, and then the Iodoform test)

- If **Brady's reagent**³ is added to a Carbonyl compound (i.e. ones that have the form “**RR' >C=O**”)⁴, then a yellowy/orangey/reddy colour appears. **Brady's reagent does not distinguish between one Carbonyl compound and another.** For **both** Aldehydes and Ketones a yellow/reddy colour appears.
- The **Iodoform** (CHI₃) test will distinguish a Ketone from an Aldehyde provided that the Ketone has a CH₃ species at one end of it (and these are called “Methyl Ketones”). **Most (but not all) Ketones will produce the fine yellow crystals of Iodoform (CHI₃) when warmed with Iodine and either Sodium or Potassium Hydroxide⁵ – but most Aldehydes (other than for Ethanal) will not do so.** However, you first need to perform Brady's test to establish that the compound in question is a **Carbonyl compound** because certain Alcohols will also test positively in the Iodoform test.

Reaction Equation for **Ketones**: $\text{RR}'>\text{C}=\text{O} + 3\text{I}_2 + 4\text{OH}^- \longrightarrow \text{CHI}_3 + \text{RCOO}^- + 3\text{I}^- + 3\text{H}_2\text{O}$

NB In forming the CHI₃ species one C atom will be **removed** from the Carbonyl chain therefore **the base name of the compound will change.**

- I very much doubt that you will be asked anything detailed about the workings of either Brady's reagent or the Iodoform (Triiodomethane) reactions, but each involves ground that we have covered and ground that you need to know at 'A' Level, so let us look at each of these reactions.
- Chemistry (as with most sciences) has to be logical, and that means that if you use the knowledge that you have, you can then derive/deduce information that you do not possess. Let us see how this works.

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

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.

³ 2,4-**Di**Nitro**P**henylhydrazine (2,4-DNP) which is sometimes also written as **2,4-DNPH**.

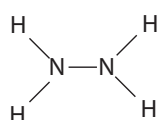
⁴ In order to distinguish one “R” species from another two conventions are used (a) R₁R₂R₃... and (b) RR'R'.

⁵ Or else with NaClO(aq) and KI(aq).

Brady's Reagent

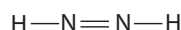
- The element Nitrogen is in Group V and thus needs to form three bonds in order to achieve the Noble Gas configuration. The most common Nitrogen compound is Ammonia, NH_3 , and the N atom has a lone pair of electrons with which it can form dative bonds – and it does precisely that in Ammonium, (NH_4^+) .
- The French word for Nitrogen is “azote”, and the English word/the label ‘*azo*’ in Chemistry is derived from the French word for Nitrogen. The word “azo” thus indicates that there is an N atom in the compound. “Diazo” means that two N atoms are involved.
- “**Hydrazine**”⁶ has the formula $\text{H}_2\text{N}-\text{NH}_2$, (as in the diagram on the left below), and “*diazine*” has the formula “ $\text{HN}=\text{NH}$ ” (“azo” gives you “Nitrogen” and “di” means “two”). The “di” does not refer to the double bond in “diazine”. (Nowadays diazine is sometimes called diimide or diimine.)

hydrazine



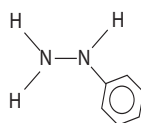
N.single bond.N

diazine or diimide or diimine



N.double bond.N

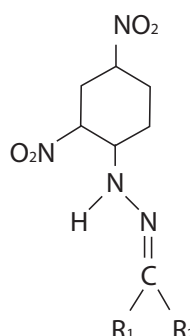
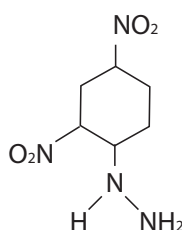
- If you replace one of the H atoms in **Hydrazine** with a Benzene ring, then you would get **Phenylhydrazine** viz. $\text{H}_2\text{N}-\text{NH}(\text{C}_6\text{H}_5)$.



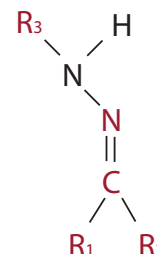
- Without looking at the next diagram, could **you** now please draw **2,4-DiNitroPhenylHydrazine** (commonly called 2,4-DNPH for short). It will remind you of the rules in the naming of Benzene compounds. (Our interest here centres on the hydrazine and not on the nitro bits.)

2,4-DiNitroPhenylHydraz**I**ne

2,4-DiNitroPhenylHydraz**O**ne



Please concentrate on the two N atoms

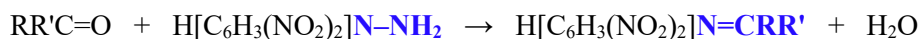


- The only difference between the “-**zine**” and the “-**zone**” is that “zine” has two H atoms attached to the bottom N atom on the right, whilst the “zone” has R_1 and R_2 attached to a C atom which is double bonded to the N atom. (“R” can be any legitimate species, but it is usually an H atom/an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

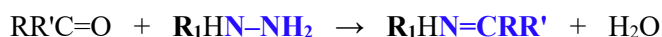
⁶ It should really be called “dihydrazine”.

NB In a recent Edexcel exam paper you were expected to know that

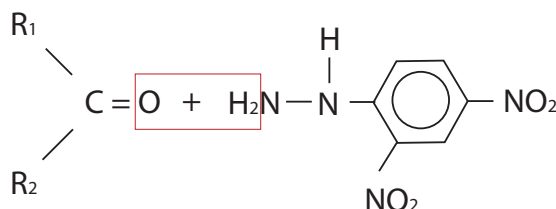
- **there is a double bond in the 2,4-DiNitroPhenylHydrazone species “-N=C ”.** Please be aware of *both* forms (the “hydrazine” and the “hydrazone” forms) of 2,4-DNPH.
- In a recent exam paper you were also expected to know that it is the unbonded/the lone pair of electrons on the 2,4-DNPH that makes it nucleophilic.
- There are other organic compounds besides Aldehydes and Ketones that contain the Carbonyl “>C=O” species (e.g. Esters/Amides/Carboxylic Acids/Acyl Chlorides) and some of these compounds will test positive for Brady’s reagent (a mixture of 2,4-DNPH/methanol/and Sulphuric Acid). **However, for ‘A’ Level exam purposes please assume that Brady’s will confirm that the organic compound is either an Aldehyde or a Ketone, and then proceed from there to distinguish the Aldehyde from the Ketone.**
- **OK, so what is Brady’s test all about? (The reagent is also known as Borche’s Reagent.)**
- Brady’s reagent consists of a mixture of 2,4-DNPH and Methanol and a little Sulphuric Acid, and it will react with a Carbonyl compound (in the equation shown below) and there will be a colour change as the “hydrazine” turns into “hydrazone” (and a molecule of water is ejected). The structural formula for the reaction is



and please note how the C₆H₆ of the Benzene ring here is C₆H₃ (because three of the H species have been replaced by other species). If you let **R₁** = [C₆H₃(NO₂)₂] , then the equation becomes

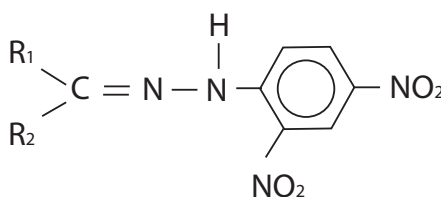


Carbonyl Compound 2,4-DNPhenylhydrazine



The Water is ejected in a condensation reaction, and 2,4-DiNitroPhenylhydrazone is formed.

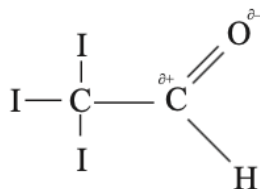
2,4-DNPhenylhydrazone



- This is an example of a “**condensation reaction**” where two molecules join together to form a larger molecule and at the same time eject a small molecule (such as Water or HCl).
- OK, this has been a little revision exercise, and at ‘A’ Level you are most unlikely to be asked anything other than to say that **Brady’s reagent will test positive for a Carbonyl compound by producing a yellow colour (or sometimes a reddish one) while the 2,4-DNPH turns from the “hydrazine” form into the “hydrazone” form.**
- Let us now take a quick look at the Iodoform/Triiodomethane reaction, and again you are not going to be asked detailed questions on this reaction – but it is an opportunity to do some revision while we are learning about Carbonyl compounds.

The Iodoform/Triiodomethane reaction

- **In general Methyl Ketones respond positively to the Iodoform test but Aldehydes (other than for Ethanal) do not.**
- One of the earliest reactions that I taught you in Organic Chemistry was the Free Radical Substitution of an Alkane – and this would be a good opportunity for you to remind yourself of the stuff in Chapter 3 of last year’s Organic Chemistry book.
- Because there are so many compounds in Chemistry, chemists were calling things by different names and this was a very unsatisfactory situation. They therefore got together and decided to create a standard way of naming chemical species, and a committee was formed to standardise naming procedures under the aegis of the International Union of Pure and Applied Chemistry (IUPAC).
- Could you please look at the name “tri-iodomethane” and draw the molecule for yourself. It will be ridiculously easy if (as the name suggests) you start with Methane and then substitute three I atoms for three H atoms in the Methane. The resulting molecule is CHI_3 , and the old name for this was Iodoform. Would it surprise you if I told you that if you did a similar thing with Chlorine instead of Iodine, then you would have got **Chloro**form (CHCl_3) instead of **Iodo**form? Chloroform was the anaesthetic that was used to render patients unconscious during surgery in the olden days.
- Ethanal will react with three molecules of Iodine to form triiodoethanal, “ $\text{CI}_3\text{—C=O(H)}$ ”, where three I atoms replace three H atoms. Please could you now draw triiodoethanal – and this is what you should have got.

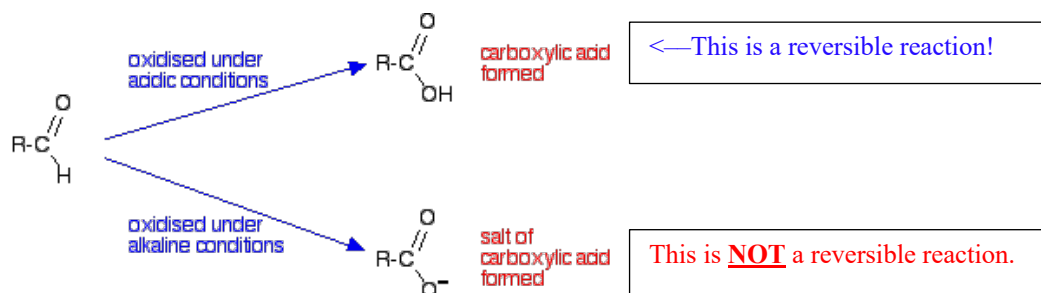


- There you have the essence of the Tri-iodomethane reaction. When you **warm any Carbonyl species that has a methyl (“ —CH_3 ”) species attached to the “C atom double-bonded to the O atom” (“ C=O ”) with Iodine in the presence of a base such as NaOH, then you get a yellow precipitate of CHI_3 .**
- In theory the **Iodoform** (CHI_3) test should distinguish a Ketone from an Aldehyde, and most (but not all) **Ketones** will produce the fine yellow crystals of CHI_3 of Iodoform (CHI_3) **when warmed with either Iodine in the presence of a base or with NaClO(aq) and KI(aq) – and most Aldehydes (other than for Ethanal) will not do so.** It is only Methyl Ketones that will do so.

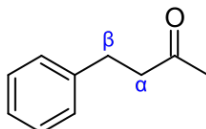
- However, the reason that I got you to draw the triiodoethanal molecule " $\text{I}_3\text{C}-\text{C}=\text{O}(\text{H})$ " was to start you off with something easy, and then to tell you that any compound with that has the form (" $\text{CH}_3-\text{C}=\text{O}(\text{R})$ ") will test positively in the Triiodomethane reaction. **If the compound has a " $-\text{CH}_3$ " species attached to the " $\text{C}=\text{O}$ " species, then the yellow precipitate of CHI_3 will be formed.**
- Actually it is even worse than that, because **ANY** compound that has the form $\text{CH}_3.\text{CH}(\text{R})(\text{OH})$ will also react with Iodine in the presence of a base such as Sodium Hydroxide to form a fine yellow precipitate. For example Ethanol will give a fine yellow precipitate in response to the Iodoform test. Some textbooks write about the reaction as though the Iodoform test will provide a definitive answer to the question "Is this an Aldehyde or a Ketone?"; but, as you have now seen, **in general Methyl Ketones respond positively to the Iodoform test but Aldehydes (other than for Ethanal) do not.** This is therefore NOT a particularly sensitive test for the purpose of definitively distinguishing Aldehydes from Ketones.

B) The Oxidisation of an Aldehyde using either Tollen's /Fehling's /or Benedict's reagents

- Jim Clark in his excellent website asks the following question: "What is formed when Aldehydes are oxidised?" and he answers his question by saying "It depends on whether the reaction is done under acidic or alkaline conditions. **Under acidic conditions, the Aldehyde is oxidised to a carboxylic acid. Under alkaline conditions, this couldn't form because it (the carboxylic acid) would react with the alkali. A salt is formed instead.**"⁷



- At 'A' Level it is better to stick to acidified oxidation (as I did in the First Year), but you now need to know about the usage of the label " α " in Organic Chemistry (as in α -hydroxy ketones).
- In Organic Chemistry the term " α " is used to refer to the first C atom that is attached to a functional group. However, although there is certainly one C atom attached to the C atom in every " $>\text{C}=\text{O}$ ", there may be two C atoms attached to the functional group C atom as there is in a Ketone. In the diagram below (from Wikipedia) there are **two** C atoms attached to the C atom in " $>\text{C}=\text{O}$ " therefore there are two alpha-C atoms and **FIVE** "alpha H atoms" in this diagram. (NB The CH_3 on the right is omitted but, nevertheless, it **is** there.)



- You will encounter the use of the label " α " very often in Biology (in peptides/chromosomes/DNA/genes/etc).

⁷ I will remind you that under reasonably gentle oxidation, Ketones are **not** oxidised. Under aggressive oxidation the Carbon to Carbon bonds rupture and acids are formed. The same is true for 3° Alcohols.

B.1) Tollen's reagent (with the formation of a silver/grey precipitate when oxidation occurs)
(It is an oxidation process therefore Aldehydes test positive, but almost all Ketones do **not** do so.)

- Tollen's is a slightly stronger **oxidising** agent than either Fehling's or Benedict's blue solutions, and (I believe) that all Aldehydes will test positive to it. However, please be aware that so will other compounds.⁸ Tollen's/Fehling's/and Benedict's solutions will all oxidise an **Aldehyde** into an **Acid**.
- At 'A' Level no reaction equation need be given, but you can say that when oxidation takes place "RCHO" (the Aldehyde) is being converted into an Acid "RCOOH".

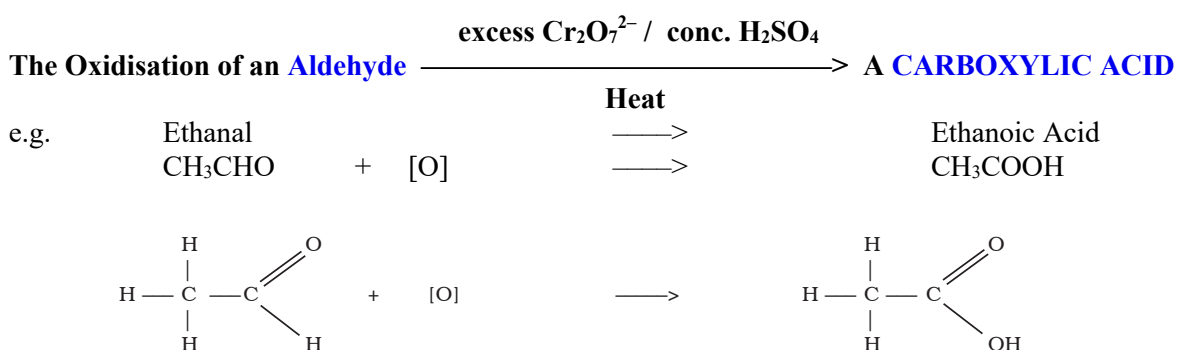
B.2 Fehling's and Benedict's blue solutions

(Again, this is a gentle oxidation reaction, therefore Aldehydes respond to the test but Ketones do not do so.)

- **Aldehydes** become oxidised to an acid and a reddy-brown Copper (I) Oxide precipitate is formed which settles to the bottom of the test-tube over a period of time to leave a clear solution. **Ketones are not easily oxidised**⁹ but please be careful because, as I have already mentioned, a lot of other things can also be oxidised.
- Fehling's is made of $[\text{CuSO}_4(\text{aq}) + \text{aqueous potassium sodium tartrate}^{10} + \text{NaOH}]$, and Benedict's solution contains a 'complex' of Cu^{2+} ions and 'ligands'. During oxidation, in both solutions the blue Cu^{2+} will be converted into a coppery/reddy-brown precipitate of the Cu^+ ions in Cu_2O .

C) The Oxidisation of an Aldehyde to the relevant Carboxylic Acid

- I covered this in very considerable detail in the first year, and I have reprinted the First Year Chapter on Alcohols in Chapter 18.
- The reaction equation is as follows (and you can use this reaction equation as an example in all your oxidation reactions)



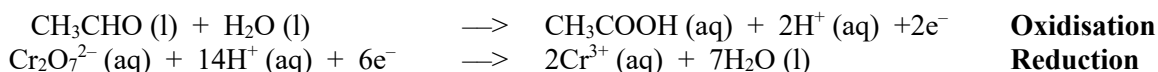
NB In a test-tube you must have an excess of $\text{Cr}_2\text{O}_7^{2-}$ otherwise you will run out of the Oxidising agent before the reaction is complete!

⁸ All α -hydroxy Ketones (i.e. Ketones where a C atom next to the C atom in “ $>C=O$ ” has an “ $-OH$ ” attached to it), and also hydroxyl amines/formic acid/and terminal alkynes will oxidise – **but do NOT bother about these.**

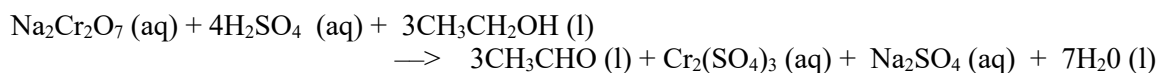
9 Mainly because of steric hindrance by the alkyl groups in Ketones blocking the approach of the oxidising agent.

¹⁰ More correctly known as Potassium sodium tartrate tetrahydrate (and it is a salt of both Sodium and Potassium).

- The Sodium or Potassium Dichromate contains the $\text{Cr}_2\text{O}_7^{2-}$ ion, and the Chromate (VI) Cr^{6+} ion has an orange colour, but the Cr (VI) ion will be *reduced* to a blue Cr (III) Cr^{3+} ion during the reaction (as it loses Oxygen to the Alcohol) – therefore as the blue Cr^{3+} ion is formed it mixes with the orange Cr^{6+} ion, and once the reaction has started, the resulting colour is green because (from your knowledge of Physics, or if you are a painter then you will know that) when orange/yellow is mixed with blue the appearance of the resulting colour is green.
- Pearson Publishing (Edexcel) give the following Redox equations. I do not believe that you will be **asked** for them in the exam, but you may be **presented** with them. The Oxidisation of the Aldehyde must be accompanied by the Reduction of the Chromate (VI) ion



- Depending on the reagents that were used, the overall reaction equation could then be something like the following. Again, you will not be asked for this reaction equation in the exam, *but you may be presented with something like it (as was the case in the OCR Organic paper in May 2002).*

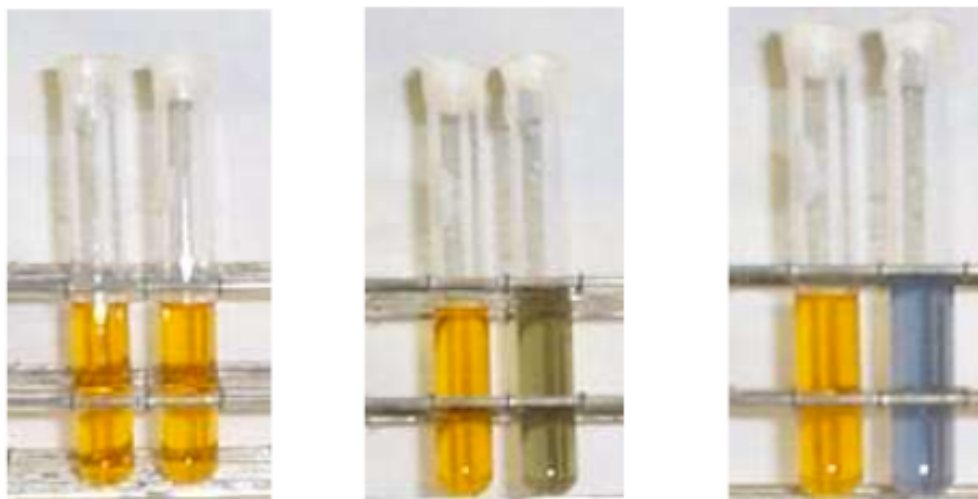


- The perception of colour is a very personal thing, and if you are using Potassium as the cation for your source of dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ions as the oxidising agent when oxidising an alcohol, then you need to know the colour change is from **orange** to **green**.
- Potassium dichromate powder has a bright orange colour and potassium chromate (CrO_4^{2-}) powder has a bright yellow colour. (Colour is a visual perception, and *to me the 'orange' below looks red and not orange.*) The colour of the liquid in the test-tubes overleaf looks brown/orange to me.



Source: https://en.wikipedia.org/wiki/Chromate_and_dichromate

- When you perform the oxidisation of an alcohol using **acidified** dichromate ions in a test-tube (it will not work without a very strong concentrated acid), then you get the following colour changes



Source: <https://projects.ncsu.edu/project/chemistrydemos/Organic/Breathalyzer.pdf> (North Carolina State University)

- The initial colour change is orange to a dirty green because there is still orange present (and blue plus orange looks green). When all the alcohol has been oxidised (and remember you must use an excess of acidified dichromate ions otherwise there is a danger that you will not complete the reaction that you have set out to observe), then the colour will be blue. That is the basis of the orange to green claim. It is actually orange to blue – but in life you must know which battles to fight and which you cannot win. **The examiners do NOT want to hear orange to blue**, they want to hear **orange to GREEN** – so give them what they want to hear.

D) The Reduction¹¹ of an Aldehyde to an Alcohol using Lithium-tetrahydrido-aluminate (LiAlH_4) or else Sodium-tetrahydrido-borate (NaBH_4)¹²

- In Chemistry, **reduction** is the contrary of oxidisation.

Can be a violent reaction with LiAlH_4

Reaction Equation: $\text{RR}'>\text{C}=\text{O} + [\text{H}] \xrightarrow{\text{or else with NaBH}_4}$ the appropriate 1° or 2° Alcohol

- Up to now, every time that I have talked about an “H” species, it has always been an “ H^+ ” species (viz. a proton i.e. the **cation** of Hydrogen), but now I must introduce to a much less common species viz. the Hydride “ H^- ” species i.e. the **anion** of Hydrogen. **The H atom prefers to be an “ H^+ ” cation rather than an “ H^- ” anion therefore the hydrides of metal compounds such as NaBH_4 and LiAlH_4 are very good **reducing** agents. (Reduction Involves the **Gain** of electrons: **OILRIG**.)**
- The proton cation, H^+ , is positively charged and it is therefore an *electrophile*, but the hydride anion, H^- , is negatively charged therefore it is attracted to a positive species and **it is thus a nucleophile** – and it is this, a negatively charged nucleophile H^- , that is attracted to and bonds with the electrophilic $\text{C}^{\delta+}$ in the carbonyl compound and reduces the $\text{C}^{\delta+}$ atom.

¹¹ 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.

¹² Solid LiAlH_4 can react explosively when it comes into contact with water. **It is more dangerous** than NaBH_4 , but LiAlH_4 can reduce more substances than can NaBH_4 .

- In our first year we oxidised Alcohols to Aldehydes and Ketones. Under **GENTLE** Oxidisation,

Primary (i.e. 1°) Alcohols \rightarrow **ALDEHYDES**, and then **ALDEHYDES** \rightarrow **CARBOXYLIC ACIDS**.

Secondary (i.e. 2°) Alcohols \rightarrow **KETONES**.

Tertiary (i.e. 3°) Alcohols : **RESIST GENTLE OXIDISATION**.

and here we are going to reverse that oxidation process.

- We will reduce Aldehydes to 1° Alcohols, and Ketones to 2° Alcohols using LiAlH_4 or NaBH_4 .
- The reaction is a **nucleophilic addition reaction** and the mechanism below is from Dr Ian Hunt's (University of Calgary) excellent Chemistry web-book.
- The Reduction of an Aldehyde to a 1° Alcohol using LiAlH_4 (or a Ketone to a 2° Alcohol).
(I personally would not use LiAlH_4 . The reaction is just too violent. I would use NaBH_4 .)

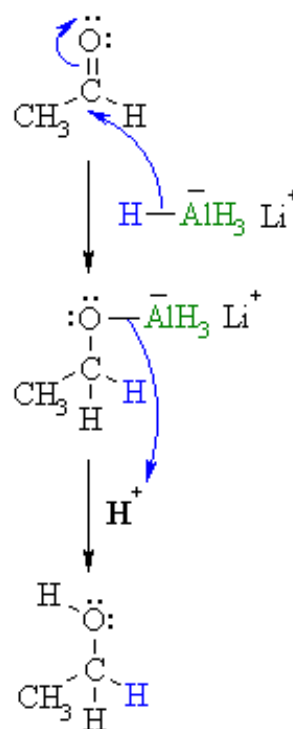
NUCLEOPHILIC ADDITION OF LiAlH_4 TO AN ALDEHYDE

Step 1:

The nucleophilic H in the hydride reagent adds to the electrophilic C in the polar carbonyl group in the aldehyde, electrons from the **C=O** move to the O creating an intermediate metal alkoxide complex. (note that all 4 of the H atoms can react)

Step 2:

This is the work-up step, a simple acid/base reaction. Protonation of the alkoxide oxygen creates the primary alcohol product from the intermediate complex.

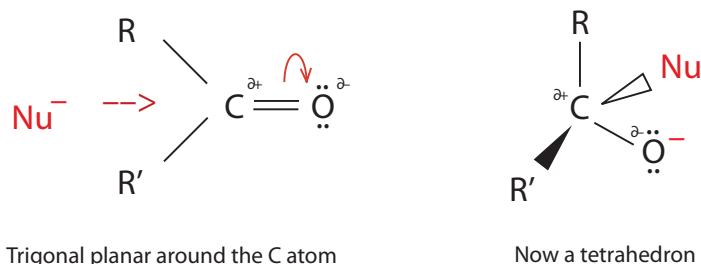


and as you can see, the starting point is an Aldehyde and the end species is an Alcohol.

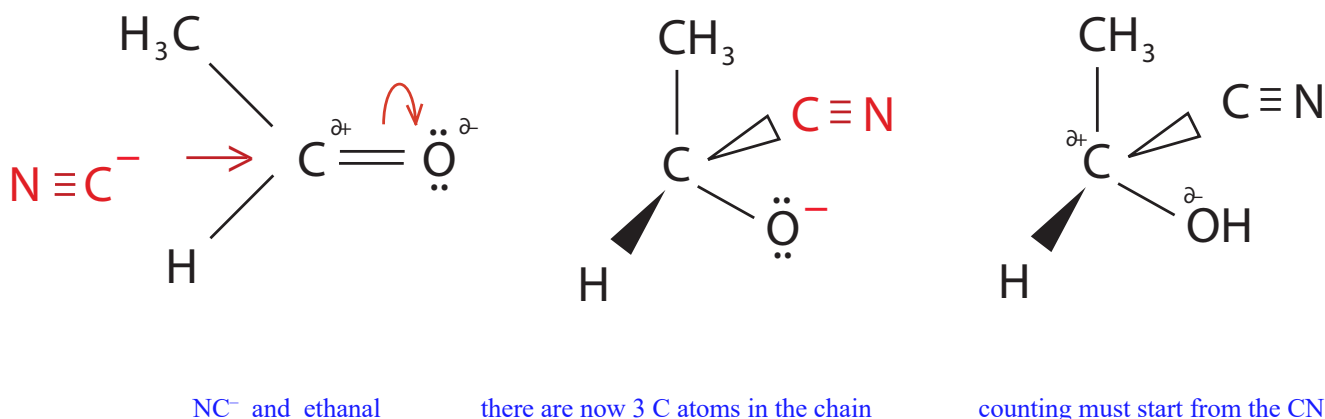
E) The Nucleophilic ADDITION reaction with Hydrogen Cyanide (HCN) to form a Nitrile
 (This reaction will take place with most Carbonyl compounds. It ADDS one C atom to the C chain.)

NB In the diagram below, the Nucleophile is CN^- . Hydrogen Cyanide, HCN, is dangerous. It is much better to use NaCN (aq) with a small amount of conc. Sulphuric Acid.

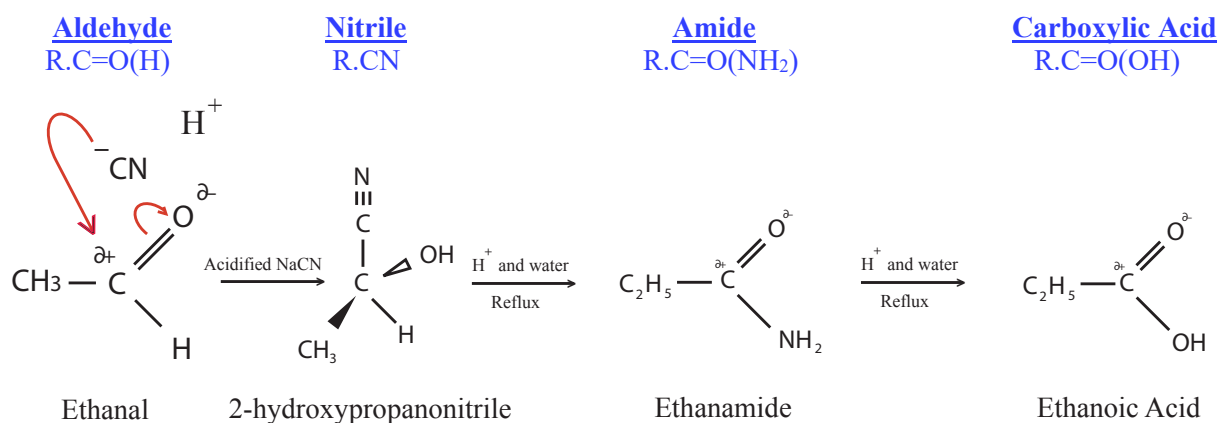
- Technically, the movement of electrons should be shown by curly arrows, but I have drawn it with a straight arrow. You can see the Nu^- , here a " $\text{C}\equiv\text{N}$ " species (with the negative charge on the C atom) attacking the $\text{C}^{\delta+}$ atom, and a **nucleophilic addition reaction** is about to take place in which the " $\text{C}=\text{O}$ " double bond will break heterolytically (and the C atom will then be attached to four species instead of three).



- The negative charge that was on the attacking nucleophile is now on the $\text{O}^{\delta-}$ atom, and the positively charged companion of the nucleophile is still hovering somewhere in the vicinity. In this part of the reaction, it has played no part.
- The " $\text{C}\equiv\text{N}$ " species can be provided by either HCN, or by acidified Sodium Cyanide (NaCN).
- With HCN, the H atom in HCN breaks away as a proton from the HCN ($\text{HCN} \longrightarrow \text{H}^+ + \text{CN}^-$), and thereby leaves its electron on the C atom to which it was attached thus leaving the " $\text{C}\equiv\text{N}$ " species (cf. below) with a lone pair of electrons, and thus the negative charge is on the C atom.
- In the diagram below, the H^+ (from the HCN) is then attracted to the O^- species in a Carbonyl species (here an Aldehyde) and bonds with it. In the middle diagram below, the double bond in the " $>\text{C}=\text{O}$ " has broken heterolytically and the negative charge in the middle species below is therefore now on the O atom. On the right below, the proton from the HCN bonds with the O^- species to form an Hydroxy/or Hydroxide species – and all this I have attempted to show.
- This is a Nucleophilic Addition reaction: $\text{RR}'>\text{C}=\text{O} + \text{HCN} \longrightarrow \text{RR}'>\text{C}\equiv\text{N}(\text{OH})$.



- The product that is formed is called a “nitrile”¹³ $R-C\equiv N$, and here it is 2-hydroxynitrile,
 $RR' > C\equiv N(OH)$.
- Please note that the Carbonyl compound started life with TWO Carbon atoms – it was Ethanal. The longest Carbon chain now has THREE Carbon atoms in it therefore it is a “propanonitrile” or “Propanenitrile”. The C atom to which the N atom is bonded must now be regarded as the first C atom in the chain of three C atoms. The second atom in the chain has an “-OH” species attached to it, therefore the name must state where the “-OH” species is located (i.e. 2-hydroxy). The structural formula can be written as $CH_3.CH(OH).C\equiv N$ and the name of the molecule is
2-hydroxy propanonitrile or 2-hydroxy propanenitrile.
- This reaction is extremely slow because HCN is a very weak acid (with a pK_a of 9.3 compared to the pK_a of 4-5 for many stronger *organic* acids¹⁴). The reaction can be speeded up by acidifying the mixture to get a pH of say 4-5. The effect of the acidification is to pull more of the electron density onto the O atom (because it is attracted to the added protons in the solution) and this makes the C atom even more δ^+ and thus *more susceptible* to an attack from a nucleophile.
- In the diagram on page 12 you will see that the C atom in stages 2 and 3 is the central atom in a tetrahedron (viz. where a Pharaoh would have been buried in his pyramid), and that this C atom has four different species attached to it. The molecule is therefore **chiral** and it will have optical isomers. The products that are formed in this reaction are therefore “racemic” i.e. they are a mixture of different optical isomers.
- I do not believe that you will be asked to draw the reaction from Aldehyde to Carboxylic Acid in the exam, but you may be presented with something similar to the set of diagrams below.



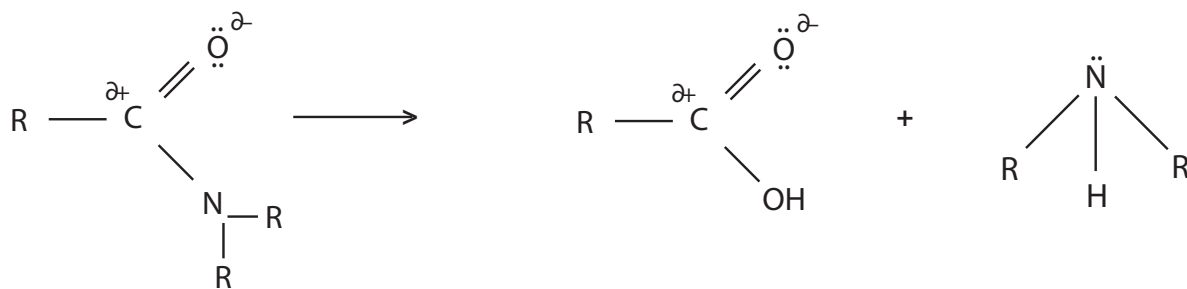
The last step above is Acid Hydrolysis from Amide to Carboxylic Acid¹⁵

NB Hydrolysis is where a molecule of water breaks the bonds in a substance and the water adds on to the substance while some other species is ejected (in the example overleaf, a secondary Amine is being ejected).

¹³ It is called the “cyanohydrin” of the Aldehyde.

¹⁴ The smaller the pK_a , the **stronger** the acid.

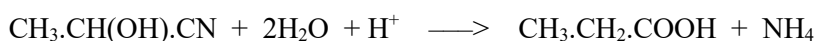
¹⁵ Acid Hydrolysis (heat with water), but Alkaline Hydrolysis with a strong base (NaOH) is another route.



- You will see the reverse of this reaction in Chapter 22.

From a Nitrile to a Carboxylic Acid

- For organic synthesis purposes, a Nitrile is a good way into a Carboxylic Acid. (NB Please remember that in going from the Aldehyde to the Nitrile, one C atom is added to the C chain. In the example on page 12 Ethanal was converted to **propanonitrile**/**propanenitrile**.¹⁶)
- I do not intend to go into this reaction in any detail because something like **14** intermediate species are involved, and all that I will say is that the conversion can be effected either through the **acid hydrolysis** of a Nitrile into a Carboxylic Acid

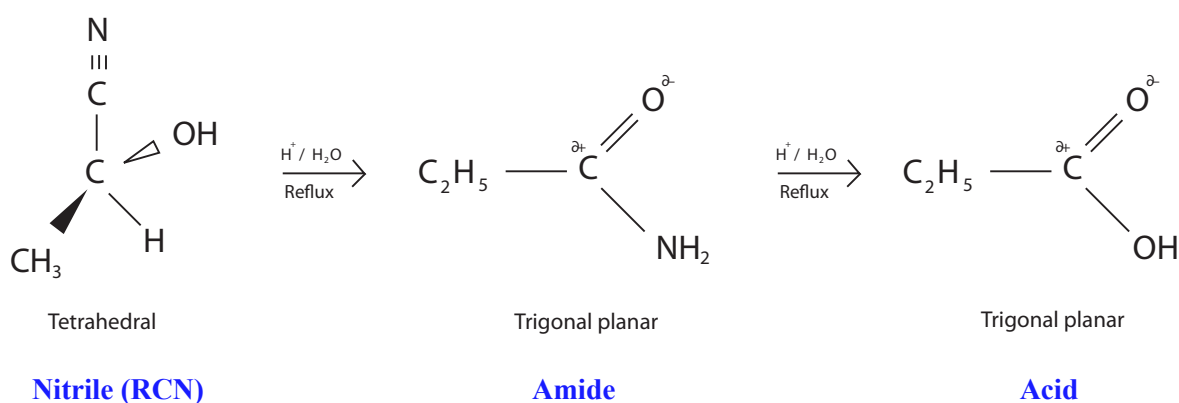


or through the **alkaline hydrolysis**



and HCl must then be added in order to convert the $\text{C}_2\text{H}_5.\text{COO}^-$ salt into the Carboxylic Acid.

- As it happens the conversion is effected through an Amide and can be summarised thus



NB This is an extremely useful conversion in organic synthesis.

¹⁶ “Propano-“ is the adjectival form of the noun “propane”.

- I have drawn an Aldehyde info tree for you on page 16, but the following are the main reactions that you need at 'A' Level.

Oxidisation Reactions of Aldehydes

- With acidified Potassium Dichromate and conc. Sulphuric Acid (just warm the mixture).
- With Tollen's reagent: warm freshly prepared AgNO_3 and NaOH *in situ* (and, generally speaking, a silver precipitate will form with an Aldehyde but not with a Ketone).
- Fehling's/Benedict's reagents (the blue Cu^{2+} ions in the solution are converted into Cu^{1+} ions and the solution turns colourless as the coppery/reddy/brown Cu^{1+} ions are precipitated).

Other Reactions of Aldehydes

- The reduction of an Aldehyde to a 1° Alcohol by LiAlH_4 or NaBH_4 .
- With Brady's reagent 2,4-DNPH, $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{NHNH}_2$ turns yellowy/orange.



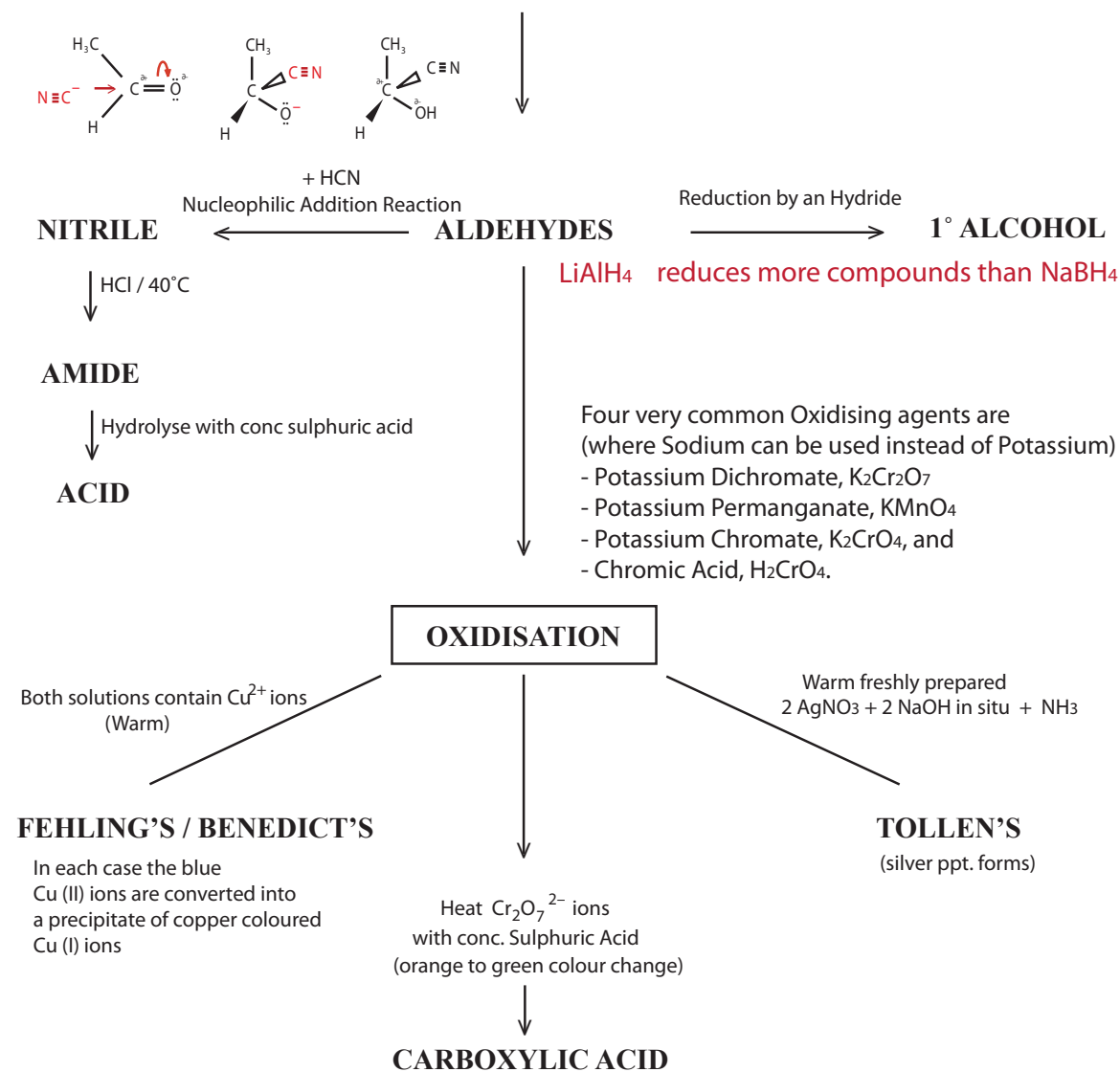
where the 2,4-DiNitroPhenylHydrazine becomes 2,4-DiNitroPhenylHydrazone.

- The Iodoform reaction with Iodine and Sodium Hydroxide to form RCOOH and yellow CHI_3 .
- With HCN or acidified NaCN to form first a Nitrile and then an Amide and then an Acid.

Two common routes into Aldehydes

- **Oxidisation of a 1° Alcohol** (with a dichromate ion/conc sulphuric acid/warm)

- **Reduction of an ester, acyl chloride or nitrile to form aldehydes**



- The following video is a lovely little demonstration by the North Carolina School of Science and Mathematics of the shifting of the position of dynamic equilibrium (Le Chatelier's Principle)
https://www.youtube.com/watch?v=_jypU3FvS_o

NB Your end-of-year exams will encompass **everything** that you have learnt in the previous two years so the video will serve to remind you of M. Henri Le Chatelier's principles.