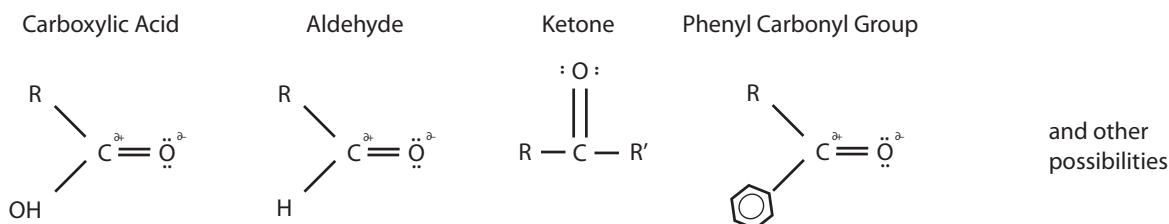


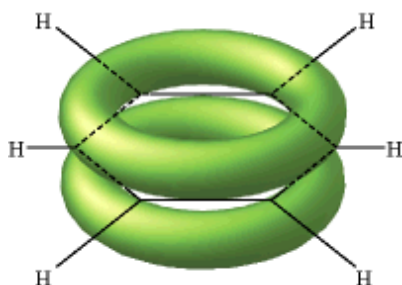
## Year 2, Organic Chemistry, Chapter 17: Carbonyl Compounds

- Carbonyl compounds have the form “ $RR'>C=O$ ” (where “R” is any legitimate group) and Carbonyl compounds typically include Carboxylic Acids/Aldehydes/Ketones/Esters/Acyl Chlorides/and also Phenyl Carbonyl compounds (4<sup>th</sup> species from the left below).

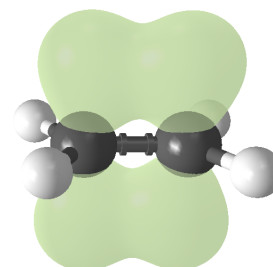


- There are **many** possible combinations of Carbonyl compounds. For example, just consider all the different possible derivatives of Benzene that could be added to ( “ $>C=O$ ” ) at one of the “R” positions. The number of possible combinations is huge, but do not lose any sleep over it because for ‘A’ Level purposes all that you need to know about are simple Aldehydes and Ketones (although there have been questions on Esters in recent years).
- In the 1950s, before we British started to go ‘abroad’ for our summer hols, many people took their holidays by the seaside (Brighton/Bournemouth/Blackpool/Bognor Regis/wherever), and it was very common for teenage girls to walk around wearing little canvas hats with the words “KISS ME QUICK” emblazoned on the hat. The message however was rather ambiguous because it could have meant “Please kiss me, but do not make it a long lingering kiss” or it could have meant “I don’t care about the length of the embrace. Just get on and do it *now*”.
- In Chemistry quite often there is very little ambiguity. Benzene molecules have a huge hoarding both above them and below them saying “Entry **only** for **ELECTROPHILES**”, and equally Alkenes such as Ethene have a big banner with the admonition “Only **electrophiles** are welcome”. Let me show you again the three-dimensional structures of each of these molecules.

[Benzene](#)



[Ethene](#)

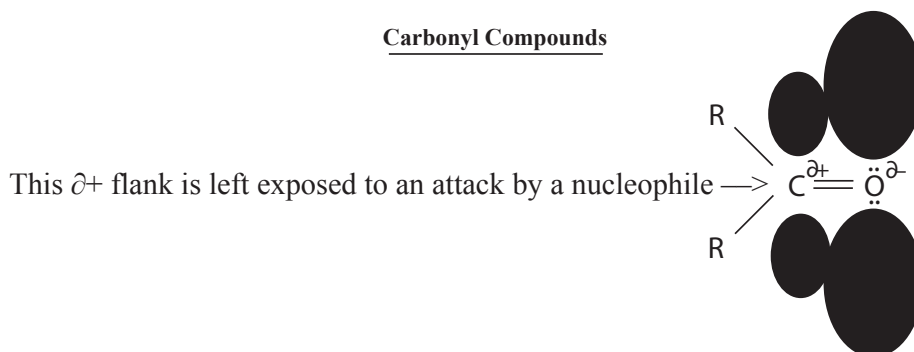


([Jiří Janoušek](#))

NB Psychologists have extensively investigated the tricks that the brain can play on perception<sup>1</sup>. Please therefore make sure that your brain distinguishes the three different horizontal planes in Benzene on the left above. The black lines should be seen as the **middle** horizontal plane.

<sup>1</sup> Please see internet pictures of Cecilia Bleasdale’s ‘famous/infamous’ dress for her daughter’s wedding.

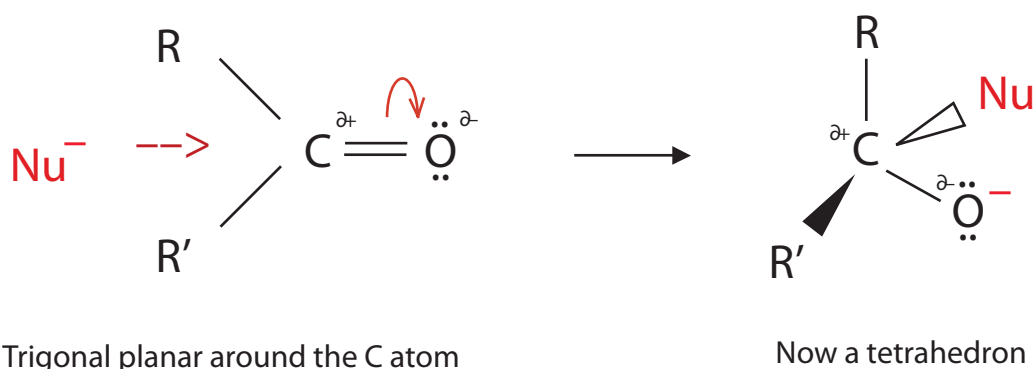
- Ignoring the extra stability possessed by Benzene, there is very little chance of a *nucleophile* reacting with Benzene because it is surrounded (both above and below) by a large delocalised  $\pi$  ring. With Ethene there is a bit more opportunity for nucleophilic attack because the protection is not quite so encompassing; but with both Benzene and Ethene there is no question – reactions that occur do so mainly with ELECTROPHILES.
- However, when it comes to Carbonyl compounds the situation is totally different. **In general, carbonyl compounds are subject to NUCLEOPHILIC reactions**, and the reason for this is as follows.
- In a Carbonyl compound the C atom is bonded to three atoms, therefore it has to form three ‘sp<sup>2</sup>’ hybridised orbitals *i.e.*  $s^1p^2$  ( $1 + 2 = 3$ ) to form three bonds leaving one unhybridised ‘p’ orbital on the C atom. The C atom uses one sp<sup>2</sup> orbital to form a  $\sigma$  bond with the O atom and the unhybridised ‘p’ orbital is used to form the  $\pi$  bond with the O atom<sup>2</sup>. The remaining two hybridised sp<sup>2</sup> orbitals are used to form the two bonds with the “R” species (cf. below).
- The O atom has two half-filled ‘p’ orbitals therefore it does not have to form any *hybridised* orbitals at all to form its two bonds. *It uses its two unhybridised ‘p’ orbitals*.
- In the Carbonyl compound below there is a  $\sigma$  bond between the C atom and the O atom, and a  $\pi$  bond above and below the plane of the  $\sigma$  bond.
- Oxygen is the second most electronegative element that there is, therefore the O atom in a Carbonyl compound pulls electron density/pulls the electron cloud off the C atom leaving the C atom as “ $\delta^+$ ” and the O atom becomes “ $\delta^-$ ”.
- I am not good with computer technology therefore I am not able to draw the situation very well – but in the diagram below I have done my best to show how the electron density has been pulled off the C atom onto the O atom thus leaving the flank of the C atom exposed to nucleophilic attack.



- In a Carbonyl compound the O atom is **much more** exposed to an attack by an **electrophile** than is the case with an Alkene species – and in many cases **an  $H^+$  species does come in and bond with the O atom** (via one of the lone pairs on the O atom), this being termed “protonation” or “**proton donation**”.
- However, the stripping of electron density off the C atom to leave it a  $C^{\delta+}$  atom has now left it very exposed to an attack by a **nucleophile** – and that is why many of the reactions of Carbonyl compounds are nucleophilic (addition) reactions. When we were talking about Benzene and Ethene in earlier Chapters, I used the term “E<sup>+</sup>” to designate an electrophile, and now I am going to use the term “Nu<sup>-</sup>” to designate a nucleophile.

<sup>2</sup> A  $\pi$  bond can never be formed with **anything other** than an unhybridised ‘p’ orbital (cf. Chapter 2).

- It does not matter what form the nucleophile takes. It is a **nucleophile** if it is
  - an electron rich species (that has a “-” charge, or a partial “ $\delta^-$ ” separation of charge)
  - that reacts with a species that contains an electron deficient area (a “+” or a “ $\delta^+$ ” area)
  - by **donating** a pair of electrons to that species, and
  - forming a covalent bond with that species.
- **In essence, a nucleophile is a donor of a pair of electrons (and indeed a nucleophile is often termed a Lewis base).**
- Technically, the movement of electrons should be shown by curly arrows, but I have drawn it below with a straight arrow. You can see the  $\text{Nu}^-$  is attacking the  $\text{C}^{\delta+}$  atom, and a **nucleophilic addition reaction** is about to take place in which the double bond will break heterolytically (and the C atom will then be attached to four species instead of three). It will no longer have any unhybridised orbitals. It will then have **four**  $\text{sp}^3$  ( $s^1p^3$ :  $1 + 3 = 4$ ) hybridised orbitals.



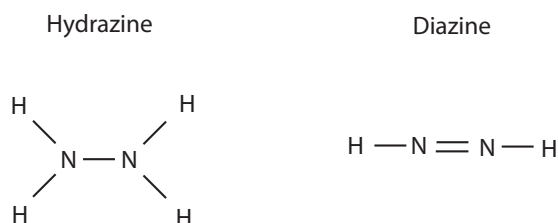
- The negative charge that was on the attacking nucleophile is now on the  $\text{O}^{\delta-}$  atom, and the positively charged companion of the nucleophile is still hovering somewhere nearby. In this part of the reaction, it has played no part.
- OK, if you have not got the picture as yet, then please go back and read the last two pages again. At ‘A’ Level, other than for proton donation, we will be concentrating on the nucleophilic reactions of Carbonyl compounds; and, actually, even without you realising it, we talked about them a huge amount last year – except that we were talking about the creation of Carbonyl compounds last year (with the colour change from orange to green in the Dichromate ions), and this year we will be talking about the reversal of those reactions.
- Last year we talked about the **oxidisation** of Alcohols into
  - Aldehydes and Carboxylic Acids from Primary Alcohols, and the formation of
  - Ketones from Secondary Alcohols, and the fact that
  - Tertiary Alcohols resisted gentle oxidisation.<sup>3</sup>
- This year I am going to start talking about the reversal of those reactions, and the reverse of oxidisation is **reduction**. (NB Please remember OILRIG.)

<sup>3</sup> Please remember that the English verb is “to oxidise” therefore the noun that derives from it is “oxidisation” and not “oxidation”. As scientists, we would rightly object very strongly if linguists were to start messing about with the rules of science – so why should we take liberties with the rules of grammar and syntax? The function of language is to convey accurately what is in one person’s head to another person’s head – and that is why there are rules in every language. Once you start breaking the rules of a language, then you open the doors to misunderstandings.

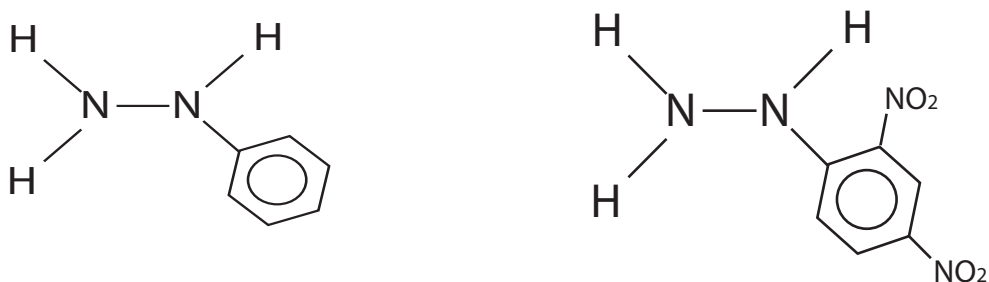
- You really do need to re-read all the First Year Chapters on Organic Chemistry because in the ‘A’ Level exams these days, you will be tested on **everything** that you have learnt in the two years prior to the exams. *Whatever, anyone may say, the Chemistry ‘A’ Level exams have become **harder** than they used to be pre-2015.*
- Last year we used the Dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) to oxidise 1° and 2° Alcohols, and I told you that we could not use a stronger oxidising agent such as  $\text{MnO}_4^-$  because 3° Alcohols resist **gentle** oxidation and  $\text{MnO}_4^-$  is not a *gentle* oxidising agent. It can rip Carbon–Carbon bonds apart!
- However, before talking about Reduction, let me say first of all that Carbonyl compounds can be identified by a test using something called “Brady’s Reagent”.

### Brady’s Reagent (a mixture of 2,4-DNPH/methanol/and Sulphuric Acid)

- 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,  $\text{NH}_3$ , and the N atom has a lone pair of electrons with which it can form dative bonds – and it does precisely that in Ammonium, ( $\text{NH}_4^+$ ).
- The French word for Nitrogen is “azote”, and the English word ‘*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**”<sup>4</sup> has the formula  $\text{H}_2\text{N}-\text{NH}_2$ , (the diagram on the left below), and “*diazine*” has the formula “ $\text{HN}=\text{NH}$ ” (“azo” gives you “Nitrogen” and “di” means “two”). Diazine can also be known as “diimine”, and the phrase “diazo” (as in diazo dyes) comes from “Diazine”.

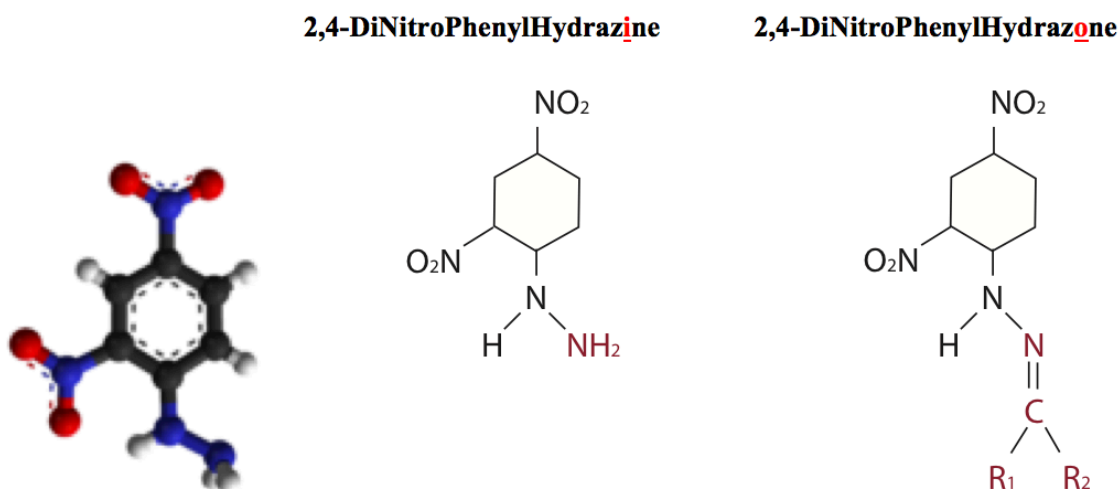


- If you replace one of the H atoms in **Hydrazine** with a Benzene ring, then you would get **Phenylhydrazine** viz.  $\text{H}_2\text{N}-\text{NH}(\text{C}_6\text{H}_5)$ , the molecule on the left below, and if you substituted two “ $-\text{NO}_2$ ” species at positions 2 and 4 then you would get **2,4-DiNitroPhenylHydrazine** (“phenyl” is the adjective for “ $-\text{C}_6\text{H}_5$ ”).



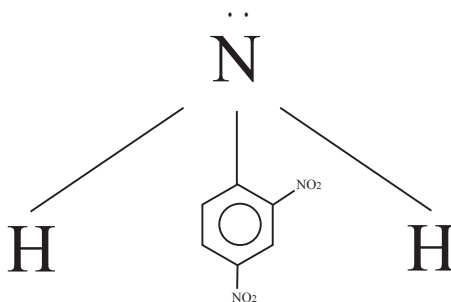
<sup>4</sup> It should really be “dihydrazine”.

- 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.



- 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<sub>1</sub> and R<sub>2</sub> 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). **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 therefore be aware of *both* forms of 2,4-DNPH.
  - In another recent exam paper you were expected to know that it is the unbonded/the lone pair of electrons on the 2,4-DNPH that makes it nucleophilic (viz. it is the lone pair of electrons that makes it a nucleophile).

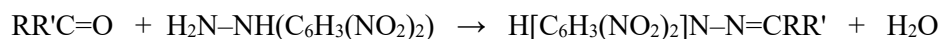
Phenylhydrazine where the emphasis is on the fact that the molecule is an AMINE.



- There are other organic compounds besides Aldehydes and Ketones that contain the Carbonyl “>C=O” species (e.g. Esters/Amides/Carboxylic Acids/Acyl Chlorides/etc) and in some circumstances an Ester (but not the other Carbonyl compounds) will test positive for Brady’s reagent but **for ‘A’ Level purposes please assume that it is only Aldehydes and Ketones that will test positive to Brady’s reagent, and then proceed from there to distinguish the Aldehyde from the Ketone.**

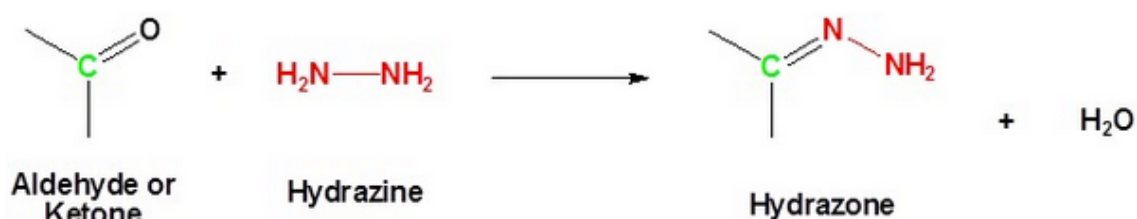
### What is Brady's Reagent and what does the test reveal?

- Brady's Reagent is a mixture of 2,4-DNPH / Methanol /and Sulphuric Acid (and all three together make up Brady's or Borsche's Reagent) and it will react with a Carbonyl compound (in the manner shown above) and there will be a colour change (**an orangey-yellow precipitate will appear in the presence of an Aldehyde or a Ketone**) as the "hydrazine" turns into "hydrazone" and a molecule of water is ejected. The equation for the reaction is



and please note how the  $\text{C}_6\text{H}_6$  of the Benzene ring here is  $\text{C}_6\text{H}_3$  (because three of the H species have been replaced by other 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



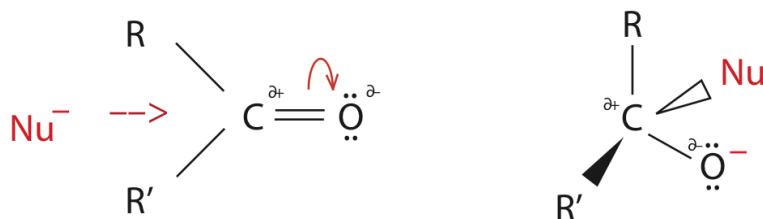
*Source: Chemistry LibreTexts*

- Brady's Reagent will thus identify an Aldehyde and a Ketone (by the appearance of the orangey-yellow precipitate), but it will not distinguish the Aldehyde from the Ketone. That requires something like Tollen's (a colourless Silver  $\text{Ag}^+$  complex solution)/Benedict's/or Fehling's solutions (both being  $\text{Cu}^{2+}$  complexes).
- OK, now let us talk about Reduction.
- Where we used  $\text{Cr}_2\text{O}_7^{2-}$  last year for oxidation, this year we are going to use Lithium Aluminium Hydride,  $\text{LiAlH}_4$  to reduce Carbonyl compounds.  $\text{NaBH}_4$  is not a strong enough reducing agent to reduce **all** Carbonyl compounds whereas  $\text{LiAlH}_4$  would be.  $\text{NaBH}_4$  will reduce a Ketone to a  $2^\circ$  Alcohol, and an Aldehyde to a  $1^\circ$  Alcohol, but  $\text{LiAlH}_4$  will reduce Esters to  $1^\circ$  Alcohols/Carboxylic Acids to  $1^\circ$  Alcohols/and Amides to  $1^\circ$  Amines. However, solid  $\text{LiAlH}_4$  **reacts violently with water and it is therefore dangerous**. I shall however quote  $\text{LiAlH}_4$  even though it is dangerous because exam boards use it.

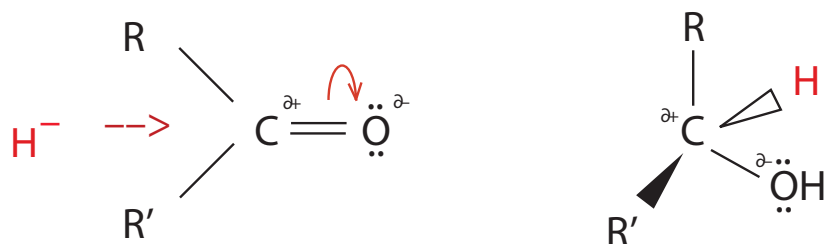
### The Reaction Mechanism in a REDUCTION reaction

*(and a question on this has appeared recently in an OCR paper)*

- $\text{LiAlH}_4$  and  $\text{NaBH}_4$  are **Hydrides**, and if an "H" species were to break away from  $\text{NaBH}_4$  or  $\text{LiAlH}_4$ , then it would do so **NOT AS A PROTON but as an "H" species. It would break away as NUCLEOPHILE!** This is extremely important because I have already told you that in a Carbonyl compound the O atom pulls so much electron density off the C atom that the C atom becomes  $\text{C}^{\delta+}$ , and it is thus susceptible to **nucleophilic attack** in which the  $\pi$  bond in " $>\text{C}=\text{O}$ " breaks leaving the  $\sigma$  bond, and the O atom then has a negative charge on it.



- **That is precisely what happens in a reduction reaction<sup>5</sup>:** (i) an “H<sup>-</sup>” nucleophile attacks the C<sup>δ+</sup> in a Carbonyl compound (ii) the double bond breaks (iii) the bonding electron pair goes to the O atom to make it “O<sup>-</sup>” (iv) the C<sup>δ+</sup> picks up the H<sup>-</sup> species that attacked the Carbonyl compound (v) the “O<sup>-</sup>” then picks up an H<sup>+</sup> species from the water in which all this is taking place ( $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ ), or to speed the whole thing up an acid could be added and the C<sup>δ+</sup> would then pick up an H<sup>+</sup> species from the acid **and thus an Aldehyde would be reduced to a 1° Alcohol and a Ketone would be reduced to a 2° Alcohol.**
- If the question appears on your exam paper, then this is what is happening and please just draw the thing in the form of a diagram – but remember to use curly arrows where I (in order to emphasise the attack by the nucleophile) have used a straight one.



- Please remember that the technique in the ‘A’ Level Chemistry exam is bang/bang/bang/bang – answer the question in bullet points and include a reaction equation wherever it is possible, and then move on to the next question. If you attempt to write an answer in grammatically correct English (as I do), then you will never finish the exam paper. Please remember also to read the question carefully. Do not give them what *you* want to give them, but instead **give them what they want to hear.**
- On earlier pages we saw that when in the presence of an excess of an acidified Dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ), provided for example by  $\text{K}_2\text{Cr}_2\text{O}_7$ , and **concentrated  $\text{H}_2\text{SO}_4$**  (*dilute sulphuric acid will not allow the reaction to occur*), the ( $\text{Cr}_2\text{O}_7^{2-}$ ) acts as an oxidising agent and provides the Alcohol with oxygen (which is written as “[O]” and the Alcohol is then converted as follows

**Primary (i.e. 1°) Alcohols** → **ALDEHYDES**, and then **ALDEHYDES** → **CARBOXYLIC ACIDS**.  
**Secondary (i.e. 2°) Alcohols** → **KETONES**.  
**Tertiary (i.e. 3°) Alcohols** : **RESIST GENTLE OXIDISATION** by ( $\text{Cr}_2\text{O}_7^{2-}$ ).

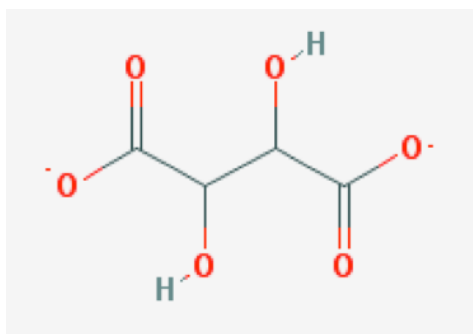
- While the Dichromate ion is providing oxygen for the oxidation to take place, the orange  $\text{Cr}^{6+}$  ion is reduced to a blue  $\text{Cr}^{3+}$  ion (and the orange/yellow and the blue coloured substances together look green). **The colour change of orange to green thus indicates where the oxidation reaction is taking place – and if there is no colour change, then no oxidation is taking place.**

<sup>5</sup> Please remember that a Reduction involves either the GAIN of electrons/or the gain of Hydrogen/or the loss of Oxygen.



### Test to distinguish an Aldehyde from a Ketone

- Let us imagine that we have three test tubes, and in each one there was just one of three Alcohols viz. a 1°, a 2°, and a 3° Alcohol, and there was a fourth test-tube with conc. sulphuric acid and the excess Potassium Dichromate in it – and all four test-tubes were in a bath of hot water. (This would get all the liquids to the same temperature).
- If one were then to put an equal amount of the acidified Dichromate into each of the test-tubes that contained the Alcohols, then two of the test-tubes would go from orange to green because
  - The 1° Alcohol would be turned into an Aldehyde (or into a Carboxylic Acid).
  - The 2° Alcohol was being turned into a Ketone, and
  - there would be no colour change in the third, because 3° Alcohols are not oxidised under these conditions.
- A lack of a colour change would thus identify the test-tube that had the 3° Alcohol in it – *but how would we know which test-tube contained the 2° Alcohol and which the 1° Alcohol?*
- Luckily there is another simple colour change that we can utilise to identify an Aldehyde from a Ketone (and thereby identify the 1° Alcohol from the 2° Alcohol). There is a substance called Fehling's **solution** and also another called Benedict's **solution**, and both of these solutions are coloured blue/cyan by the dissolved copper sulphate  $\text{Cu}^{2+}$  (aq) ions in them.<sup>6</sup>
- Both substances (Fehling's and Benedict's) are oxidising agents and will oxidise the Aldehyde into a Carboxylic Acid **but will not oxidise the Ketone into anything** – and (by definition) the oxidising agents themselves will thus be reduced from soluble  $\text{Cu}^{2+}$  sulphate ions to (in this case) insoluble  $\text{Cu}^+$  oxide ions, and thus the  $\text{Cu}^+$  ions precipitate out to give a dirty reddy-brown solution initially (but given time, the copper oxide particles will settle at the bottom of the test-tube to leave a colourless solution).
- Having identified the 3° Alcohol by the lack of a colour change from orange to green, we can then identify the 1° Alcohol by the colour change from blue to dirty reddy-brown, and the 2° Alcohol will be in the test-tube where the blue coloured solution has not altered.
- If (when talking about Fehling's solution) an exam question talks about 2,3-dihydroxybutanedioate ions, then this is what such a species looks like (where there is an Ester " $-\text{C}=\text{O}(\text{O}-)$ " bit at each end).

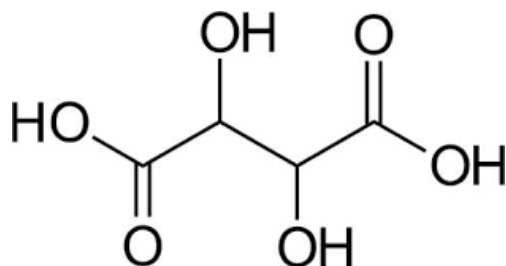


and it comes from 2,3-dihydroxybutanedioic acid which contains one acid functional group ( $-\text{COOH}$ ) at each end of the molecule (and two Alcohol functional groups in the middle of the molecule).

---

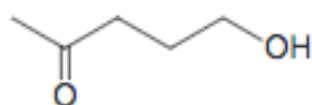
<sup>6</sup> Both solutions involve “complexes” and “ligands” and we will talk about complexes and ligands in Inorganic Chemistry in the Chapter on Transition Metals (Chapter 12). You need  $(\text{OH})^-$  ions in both the Fehling's and Benedict's complex, and we will talk about how this is achieved.



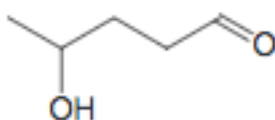


Source: [https://en.wikipedia.org/wiki/Tartaric\\_acid](https://en.wikipedia.org/wiki/Tartaric_acid)

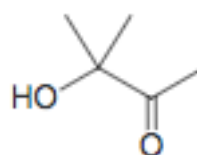
- The June OCR “Rings, Polymers and Analysis” exam paper had a question about how to distinguish one Carbonyl Group from another. You were given the three species/compounds (below) and you were asked to distinguish one from another.



compound C



compound D



compound E

- If you examine the three species (and please remember that in skeletal diagrams the “C–H” bonds are not shown) you will see that D is an Aldehyde with a **secondary Alcohol** attached to it. (It is 4-hydroxypentanaldehyde.) C is a Ketone with a **primary Alcohol** attached to it. (It is 5-hydroxypentan-2-one.) E is a Ketone with a **tertiary Alcohol** attached to it because the C atom that is attached to the “–OH” species is attached to three C atoms. (It is 3-hydroxy-3-methylbutan-2-one.)
- Ketones cannot be oxidised further but an Aldehyde (a Carbonyl compound) will react with Tollens’ reagent to form a silver precipitate and with either Benedict’s or Fehling’s solutions to form the brown-red Copper ( $\text{Cu}^+$ ) oxide ion. Tollens’/Benedict’s/or Fehling’s will therefore distinguish **D** from C and E.
- How then can C be distinguished from E? Well, a  $2^\circ$  Alcohol will oxidise into a Ketone, but a  $3^\circ$  will resist gentle oxidation, therefore if you react both with concentrated Sulphuric Acid and Sodium or Potassium Dichromate, then the solution will turn from orange to green for C, but nothing will happen with E – and now you have distinguished all three compounds from each other.
- The next couple of Chapters are about Aldehydes and Ketones.