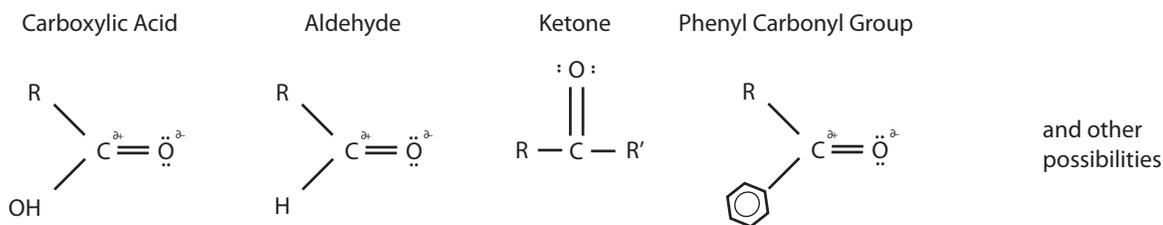


A Second Year blog on Carbonyl Compounds: Part 2, Aldehydes, 19th Jan 2019

(There is a considerable amount of **revision** in this blog. The material is in the Second Year Organic Book.)

Next to Benzene, Carbonyl compounds are probably the second most examined topic in 'A' Level Organic Chemistry. Carbonyl compounds have the form "**RR' >C=O**" (where "**R**" and "**R'**" are any legitimate species, and the "**>C=**" conveys a C atom with 4 bonds, with one of them being a double bond), and Carbonyl compounds typically include Carboxylic Acids/ Aldehydes/ Ketones/ Esters/ Amides/ Acyl Chlorides/ Acid Anhydrides/ and Phenyl Carbonyl compounds (second from right below)/etc. NB Anything that has the form "**RR' >C=O**" will have the Carbonyl "**C^{δ+}=O^{δ-}**" configuration in it.



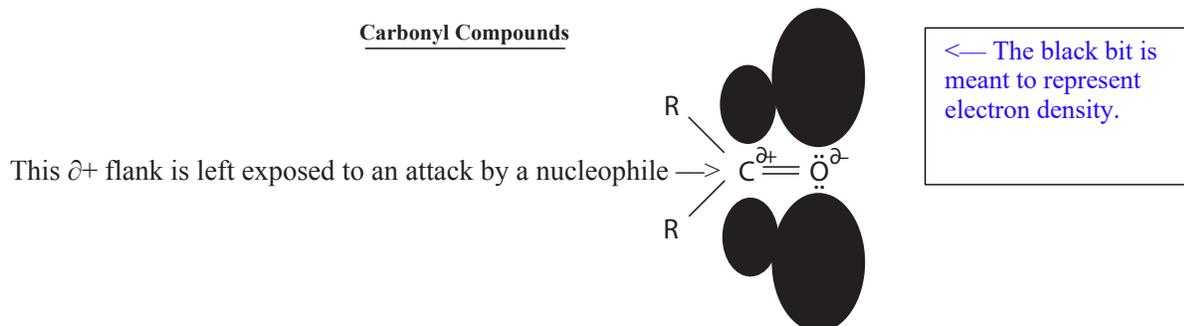
This is how Chemistry LibreTexts shows some of the Carbonyl compounds. (An "Enone" is an Alkene conjugated to a Ketone. It does **not** form any part of the UK 'A' Level syllabus.) The symbol "X" is very often used to represent a Halogen species.

Compound	Aldehyde	Ketone	Formaldehyde	Carboxylic Acid	Ester	Amide	Enone	Acyl Halide	Acid Anhydride
Structure									
General Formula	RCHO	RCOR'	CH ₂ O	RCOOH	RCOOR'	RCONR'R''	RC(O)C(R')CR''R'''	RCOX	(RCO) ₂ O

Please remember that you cannot write Aldehydes as ending in "-OH" because that would convey the impression that they were alcohols. **Aldehydes (RCHO) have to be written as ending in "-HO"**.

Ignoring the extra stability possessed by Benzene, there is very little chance of a *nucleophile* reacting with Benzene because Benzene is surrounded (both above and below) by a large delocalised π ring. With an Alkene there is a bit more opportunity for nucleophilic attack because the protection is not quite so encompassing; but with both Benzene and an Alkene there is no question – **reactions that occur do so mainly as electrophilic reactions**. However, when it comes to Carbonyl compounds the situation is the *opposite*. **In general, carbonyl compounds are subject to NUCLEOPHILIC reactions.**

Carbonyl compounds are subject to Nucleophilic Attack

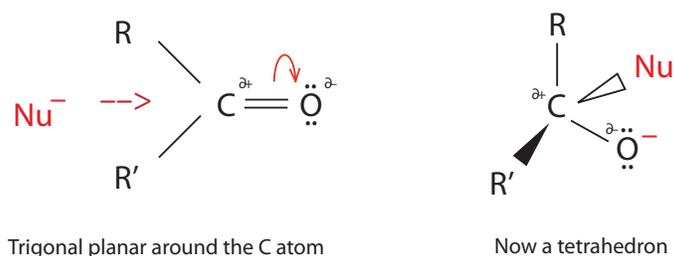


It does not matter what form the nucleophile takes. It is a **nucleophile** if it is

- an electron rich species (that has a “-” charge, or a partial “ δ^- ” separation of charge)
- that reacts with a species that contains an electron deficient area (a “+” / a “ δ^+ ” area / an empty orbital)
- by **donating** a pair of electrons to that species, and
- forming a (dative) 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 here with a straight arrow. You can see the 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 to three species).



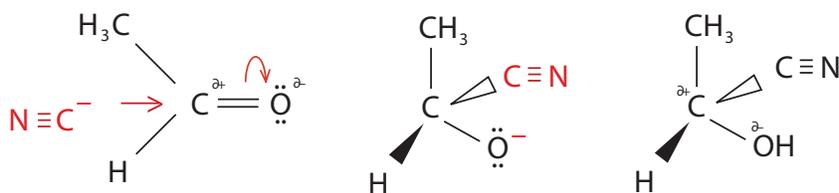
Please note that even though I have not shown all the steps in the mechanism, that

- the negative charge has moved from the nucleophile to the O atom, and
- that if the nucleophile had “n” C atoms in it, then the species on the right would now have “n” more C atoms in it than it previously had (i.e. “n” C atoms will have been added to the molecule).

For example, if the nucleophile were a “ CN^- ” species from HCN where



then this is what would happen (*with the “H” from the HCN joining on in the last step*).



The substance above has changed from an **Aldehyde** (Ethanal) to a **Nitrile** (2-hydroxy propanonitrile), and from a two-Carbon chain (**eth**anal) to a three-Carbon chain (an hydroxy**prop**anonitrile).

HCN goes under the guise of different names viz. Hydrogen Cyanide/Hydrocyanic Acid/and Prussic Acid, and it is a very weak acid. In aqueous solution it dissociates as follows



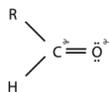
but the negative charge is actually on the C atom and not on the N atom¹. You can see this if you draw HCN.



¹ I did warn you that we chemists are not as robust scientists as Mathematicians and Physicists are. You could **not** get away with this sort of sloppiness in Maths. If you were to put your negative signs in the wrong place in Maths all your answers would be wrong – *and yet we do it all the time in Chemistry*.

ALDEHYDES



An Aldehyde can be portrayed as  or as . I prefer the first depiction because it shows the polarisation of the double bond between the C atom and the O atom, and that makes it very clear that the substance is open to nucleophilic attack, and this can be seen in the classic conversion of an Aldehyde into a Carboxylic Acid (which is not a part of the First Year Organic Syllabus but it is a part of the Second Year Syllabus). For 'A' Level, the two main reactions undergone by Aldehydes are **Oxidisation** and **Nitration**.

In the First Year we oxidised Alcohols to Aldehydes and Ketones, and under **GENTLE** Oxidisation,

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**.

The conversion from an Alcohol to a Carbonyl compound is often tested in the exams (and the colour change that they want is orange to green for 1° and 2° Alcohols, and no colour change for 3° alcohols).

Gentle oxidation involves the use of the dichromate ion oxidising agent, $\text{Cr}_2\text{O}_7^{2-}$, from Potassium Dichromate. (*The Manganate ion, MnO_4^- , would be too aggressive an oxidising agent.*) This sequence of events from an Alcohol to a Carboxylic Acid is tested by the examiners by way of the orange to green colour change and then by any one of three tests viz. Tollen's/Brady's/and Fehling's.

The Oxidisation of Aldehydes into Carboxylic Acids

- With acidified **Potassium Dichromate** and concentrated Sulphuric Acid (just warm the mixture and it will turn from orange to green).
- With **Tollen's** reagent: add AgNO_3 and NaOH *in situ*, and 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).
- **Fehling's** or **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).

As an Aldehyde oxidises into a Carboxylic Acid, it loses electrons that are taken up by the **Tollen's** or the **Fehling's** or the **Benedict's** reagent.

Brady's reagent is an important test for a Carbonyl compound. If Brady's reagent² is added to a Carbonyl compound, 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 yellowy-reddy colour (sometimes called "straw-coloured") appears.

To then distinguish an Aldehyde from a Ketone, the **Iodoform** (CHI_3) test will in most cases distinguish a Ketone from an Aldehyde provided that the Ketone has a CH_3 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 (CHI_3) when warmed with Iodine and either Sodium or Potassium Hydroxide³ – but most Aldehydes (other than for Ethanal) will **not** do so. However, **you do 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**.

² 2,4-DiNitroPhenylhydrazine (2,4-DNP) which is sometimes also written as **2,4-DNPH**.

³ Or else with $\text{NaClO}(\text{aq})$ and $\text{KI}(\text{aq})$.

Brady's Reagent

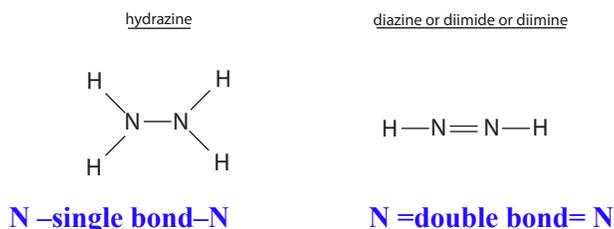
(Brady's reagent consists of a mixture of 2,4-DNPH and Methanol and a little Sulphuric Acid.)

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, 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^+).

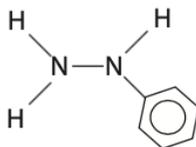
The French word for Nitrogen is “azote”, and the English label ‘*azo*’ in Chemistry is derived from the French word for Nitrogen. The term “azo” thus indicates that there is an N atom in the compound. “Diazo” means that two N atoms are involved.

diazine is also called diimide or diimine.

“**Hydrazine**”⁴ 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” comes from the Greek word for twice). The “di” does not refer to the double bond in “diazine”. Nowadays



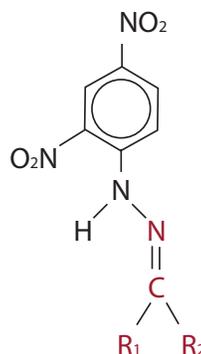
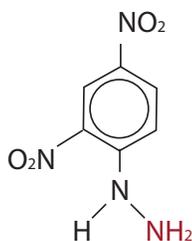
If you replace one of the H atoms in **Hydrazine** with a Benzene ring, then you would get **Phenylhydrazine** viz. $\text{H}_2\text{N}-\text{NH}(\text{C}_6\text{H}_5)$.



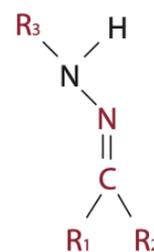
Without looking at the next diagram, could **you** now please draw **2,4-DiNitroPhenylHydrazine** (commonly called **2,4-DNPH** for short). It will remind you of the rules in the naming of Benzene compounds. (Our interest here centres on the hydrazine and not on the nitro bits.)

2,4-DiNitroPhenylHydrazine

2,4-DiNitroPhenylHydrazone



Please concentrate on the two N atoms



The only difference between the “–zine” and the “–zone” is that the “–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). ‘ R_3 ’ is the phenyl bit.

⁴ It should really be called “dihydrazine”.

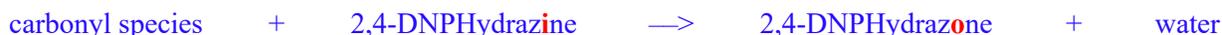
NB In a recent Edexcel exam paper you were expected to know that

- **there is a double bond in the 2,4-DiNitroPhenylHydrazone species “-N=C”**. Please therefore be aware of *both* forms i.e. the “hydrazine” (with the single “-N-N-” bond) and the “hydrazone” (with the double “-N=C-” bond) 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/etc) 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? (NB The reagent is also known as Borche’s Reagent.)

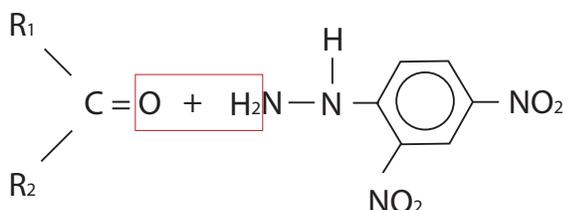
Brady’s reagent consists of a mixture of 2,4-DNPH and Methanol and a little Sulphuric Acid, and it will react with a Carbonyl compound (in the equation shown below) and there will be a colour change as the “hydrazine” turns into “hydrazone” (and a molecule of water is ejected). The reaction is



and please note how the C₆H₆ of the Benzene ring here is C₆H₃ (because three of the H species on the Benzene ring have been replaced by other species).

Carbonyl Compound

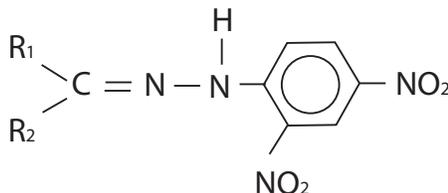
2,4-DNPHydrazine



This is a typical condensation reaction where the “O” plus the “H₂” (that I have drawn in a red box) forms water, H₂O.

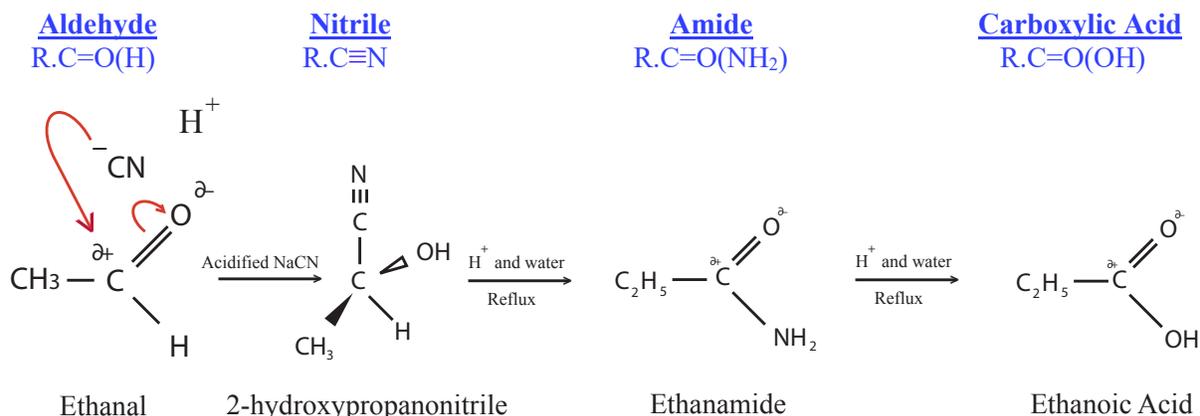
The Water is ejected in a condensation reaction, and 2,4-DiNitroPhenylhydrazone is formed.

2,4-DNPHydrazone



The numbers “2,4” indicate the positions where the Nitration occurs on the Benzene ring.

Converting an Aldehyde into a Nitrile and then into an Amide and then into a Carboxylic Acid

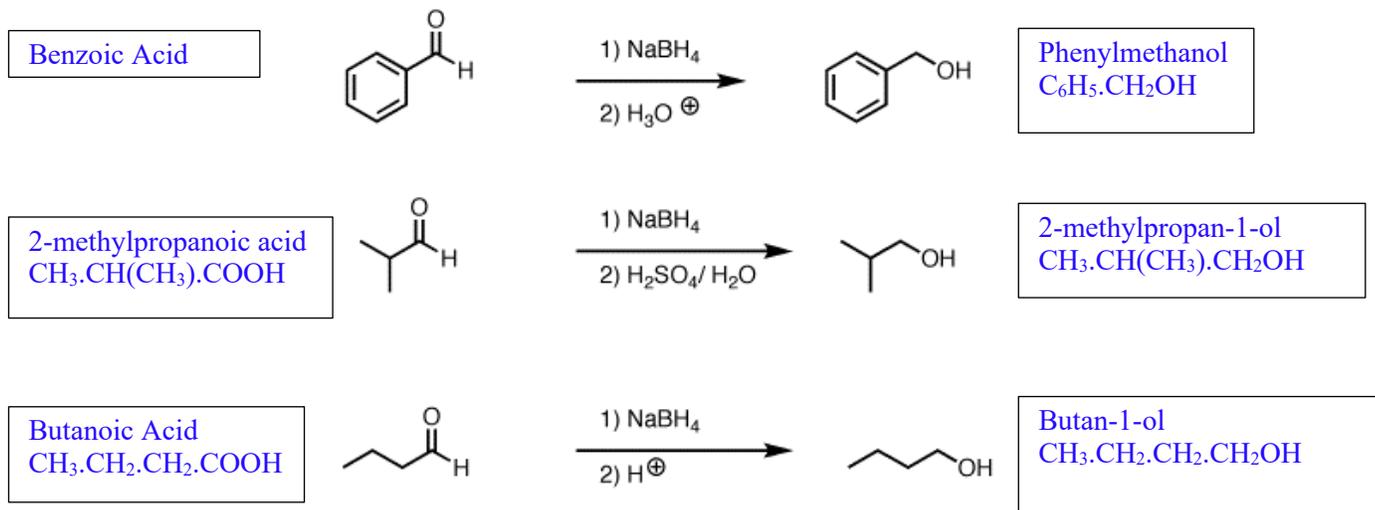


The **Nucleophilic Addition** reaction of an Aldehyde with Hydrogen Cyanide (HCN) will create a Nitrile – and for Organic Synthesis it is sensible to know that Nitriles can be reacted (with *dilute* Hydrochloric acid) to form the appropriate Carboxylic Acid.

The Reduction of an Aldehyde into a 1° Alcohol

In the First Year we saw how a 1° Alcohol was oxidised into an Aldehyde, and in the Second Year we see how to reverse the process and reduce an Aldehyde into a 1° Alcohol (and a Ketone would correspondingly be reduced to a 2° Alcohol). A Carboxylic Acid would of course be reduced first to an Aldehyde and then to a 1° Alcohol.

The two main reducing agents here are Lithium Aluminium Hydride (LiAlH₄) and Sodium BoroHydride (NaBH₄). LiAlH₄ is a more powerful reducing agent than NaBH₄, but please do be careful because it can exhibit somewhat violent reactions. Dr James Ashenurst of “Master Organic Chemistry” shows some examples of the reduction with either NaBH₄ or LiAlH₄ thus.



I think that that is enough on Aldehydes, but let me sum it up in an info tree.

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**

