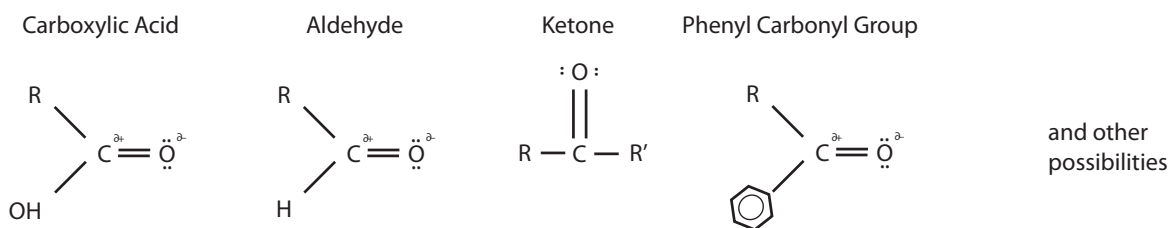








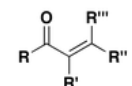

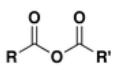
## A Second Year blog on Carbonyl Compounds: Part 3 Ketones, 19<sup>th</sup> Jan 2019

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

Carbonyl compounds have the form “ $RR'>C=O$ ” (where “R” and “R'” are any legitimate group, and the “ $>C=$ ” shows 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/ Phenyl Carbonyl compounds/etc – and anything that has the form “ $RR'>C=O$ ” will have the “ $C^{\delta+}=O^{\delta-}$ ” configuration in it.



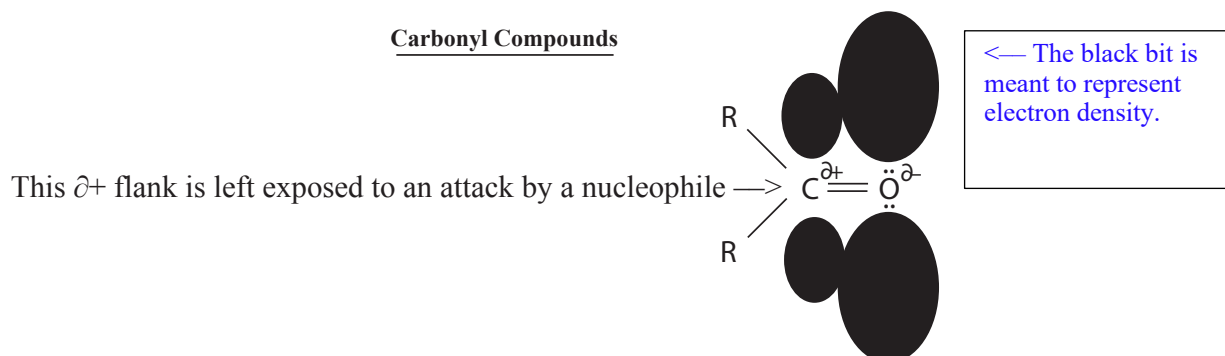
This is how Chemistry LibreTexts shows some of the Carbonyl compounds.

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

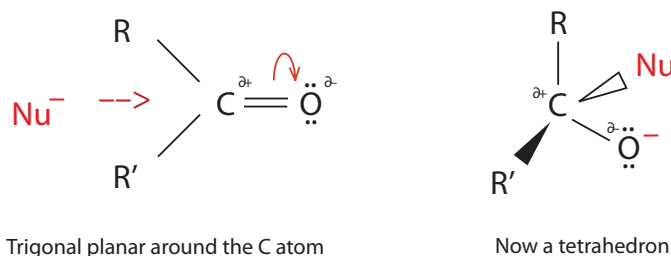


It does not matter what form the nucleophile takes. It is a **nucleophile** if it is

- an electron rich species (that has a “-” charge, or a partial “ $\delta^-$ ” separation of charge)
- that reacts with a species that contains an electron deficient area (a “+” / a “ $\delta^+$ ” 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).**

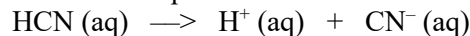
Technically, the movement of electrons should be shown by curly arrows, but I have drawn it here with a straight arrow. You can see the  $\text{Nu}^-$  is attacking the  $\text{C}^{\delta+}$  atom, and a **nucleophilic addition reaction** is about to take place in which the double bond will break heterolytically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



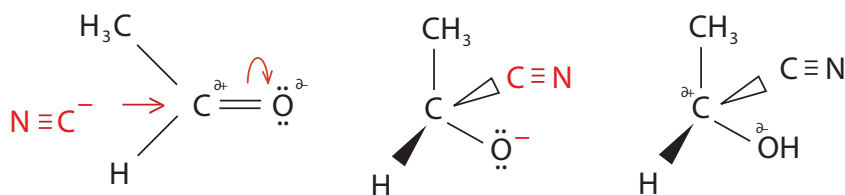
Please note that even though I have not shown all the steps in the mechanism, that

- 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 “ $\text{CN}^-$ ” species from HCN where



then this is what would happen (*with the “ $\text{H}^+$ ” from the HCN joining on in the last step*).

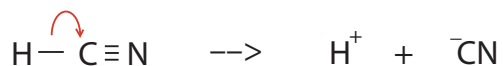


The substance above has changed from an **Aldehyde** (Ethanal) to a **Nitrile** (2-hydroxy propanonitrile), and from a two-Carbon chain (**ethanal**) to a three-Carbon chain (an hydroxy**propanonitrile**).

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



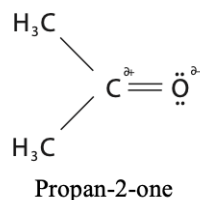
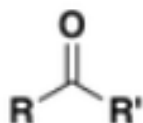
but the negative charge is actually on the C atom and not on the N atom<sup>1</sup>. You can see this if you draw HCN.



<sup>1</sup> 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, then all your answers would be wrong – *and yet we do it all the time in Chemistry*.

## KETONES

A Ketone has the following structure



The Ketone on the right is the simplest Ketone that there is. It is called propan-2-one (“prop” because the longest Carbon chain has three C atoms in it), and the “2” indicates the location of the Carbonyl species in the chain. (Its common name is acetone). The names of all Ketones end in “-one”, and the number in the name indicates where the Carbonyl species “>C=O” is located on the longest Carbon chain. The name must give the lowest number possible for the location of the Carbonyl species. The name of  $\text{C}_3\text{H}_7-(\text{C}=\text{O})-\text{CH}_3$  is thus “Pentan-2-one” and not “Pentan-4-one”.

A Secondary Alcohol will oxidise into a Ketone and, in general, Ketones do not convert into a Carboxylic Acid under gentle oxidation i.e. using a dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ), but the use of the more aggressive Manganate ion ( $\text{MnO}_4^-$ ) can be disruptive and break Carbon to Carbon bonds, and thereby create differing Carboxylic Acids.

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

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

Secondary (i.e.  $2^\circ$ ) Alcohols  $\rightarrow$  **KETONES**.

Tertiary (i.e.  $3^\circ$ ) Alcohols : RESIST GENTLE OXIDISATION.

The conversion from an Alcohol to a Carbonyl compound is often tested in the exams (and the colour change is orange to green for  $1^\circ$  and  $2^\circ$  Alcohols, and no colour change for  $3^\circ$  alcohols).

Brady’s reagent is used to test for the presence of any Carbonyl compound, but if in the exams you are given three different Alcohols (a  $1^\circ$  / a  $2^\circ$  / and a  $3^\circ$  Alcohol) and you were told that under gentle oxidation, in two of them the colour change that occurred was orange to green, and you were then asked to confirm that the resulting substances were either an Aldehyde or a Ketone, then you would use Brady’s reagent to confirm the presence of a Carbonyl compound. You could then distinguish the Aldehyde from the Ketone by way of Tollen’s / Fehling’s / or Benedict’s tests. These tests exploit the fact that an Aldehyde can be oxidised into a Carboxylic Acid whereas a Ketone resists gentle oxidation.

**Brady’s reagent** is the test for a Carbonyl compound. If Brady’s reagent<sup>2</sup> 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** ( $\text{CHI}_3$ ) test will in most cases distinguish a Ketone from an Aldehyde provided that the Ketone has a  $\text{CH}_3$  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 ( $\text{CHI}_3$ ) when warmed with Iodine and either Sodium or Potassium Hydroxide<sup>3</sup> – 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 actually a Carbonyl compound because certain Alcohols will also test positively in the Iodoform test.**

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

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

## Brady's Reagent

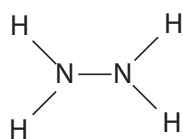
(Brady's reagent consists of a mixture of 2,4-DNPH and Methanol and a little Sulphuric Acid.)

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,  $\text{NH}_3$ , 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 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.

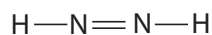
“Hydrazine”<sup>4</sup> has the formula  $\text{H}_2\text{N}-\text{NH}_2$ , (as in the diagram on the left below), and “diazine” has the formula “ $\text{HN}=\text{NH}$ ” (“azo” gives you “Nitrogen” and “di” comes from the Greek word for twice). The “di” does not refer to the double bond in “diazine”. Nowadays diazine is also called diimide or diimine.

hydrazine



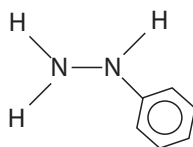
**N –single bond–N**

diazine or diimide or diimine



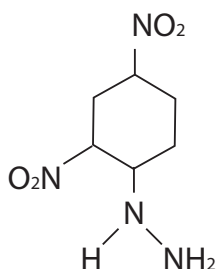
**N =double bond= N**

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

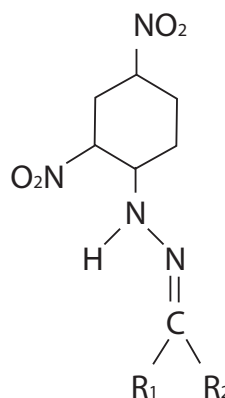


- Without looking at the next diagram, could **you** now please draw **2,4-DiNitroPhenylHydrazine** (commonly called **2,4-DNPH** for short). It will remind you of the rules in the naming of Benzene compounds. Our interest here centres on the hydrazine and not on the nitro bits. In the diagram on the right (below), “**R<sub>3</sub>**” is the phenyl bit.

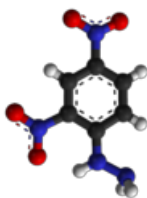
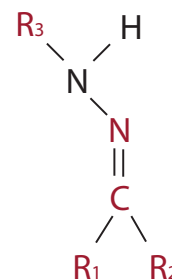
**2,4-DiNitroPhenylHydrazine**



**2,4-DiNitroPhenylHydrazine**



Please concentrate on the two N atoms

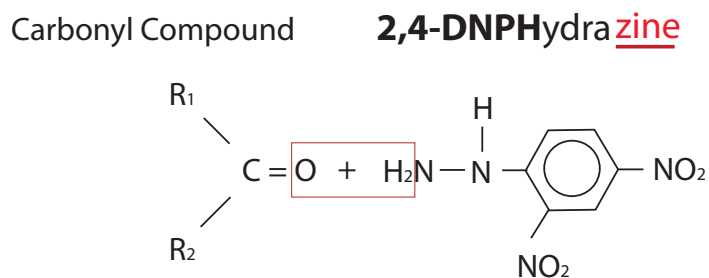


<sup>4</sup> It should really be called “dihydrazine”.

- 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 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 (using Fehling’s/Tollens’/or Benedict’s tests).**
- 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

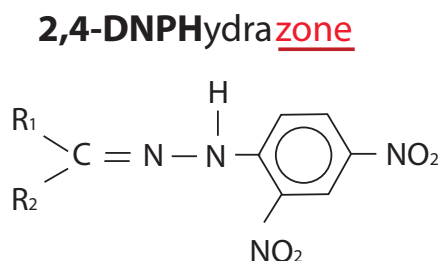


and please note how the C<sub>6</sub>H<sub>6</sub> of the Benzene ring here is C<sub>6</sub>H<sub>3</sub> (because three of the H species on the Benzene ring have been replaced by other species).



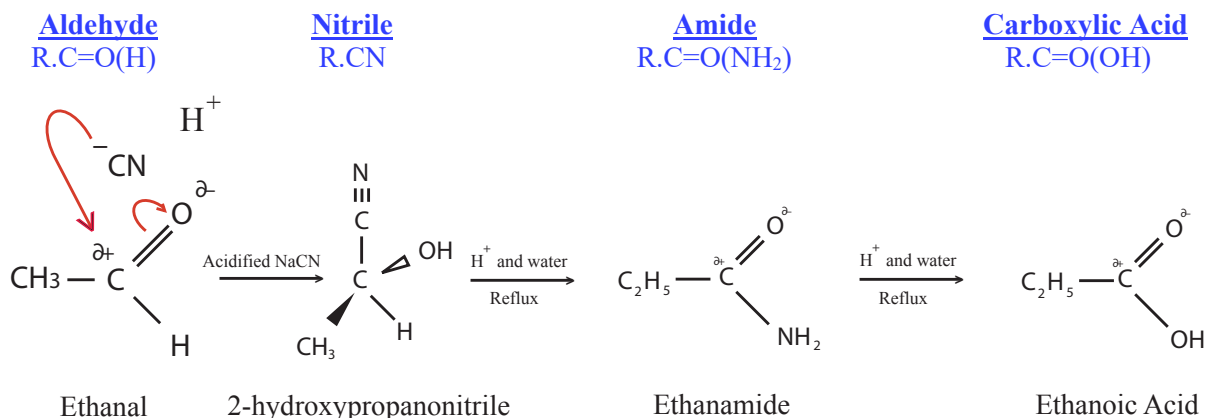
This is a typical condensation reaction where the “O” plus the “H<sub>2</sub>” (that I have drawn in a red box) forms water, H<sub>2</sub>O.

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



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

**Converting an Ketone into a Nitrile and then an Amide and then into a Carboxylic Acid**  
**(HCN is very toxic. Instead use NaCN or KCN and some dilute H<sub>2</sub>SO<sub>4</sub>.)**

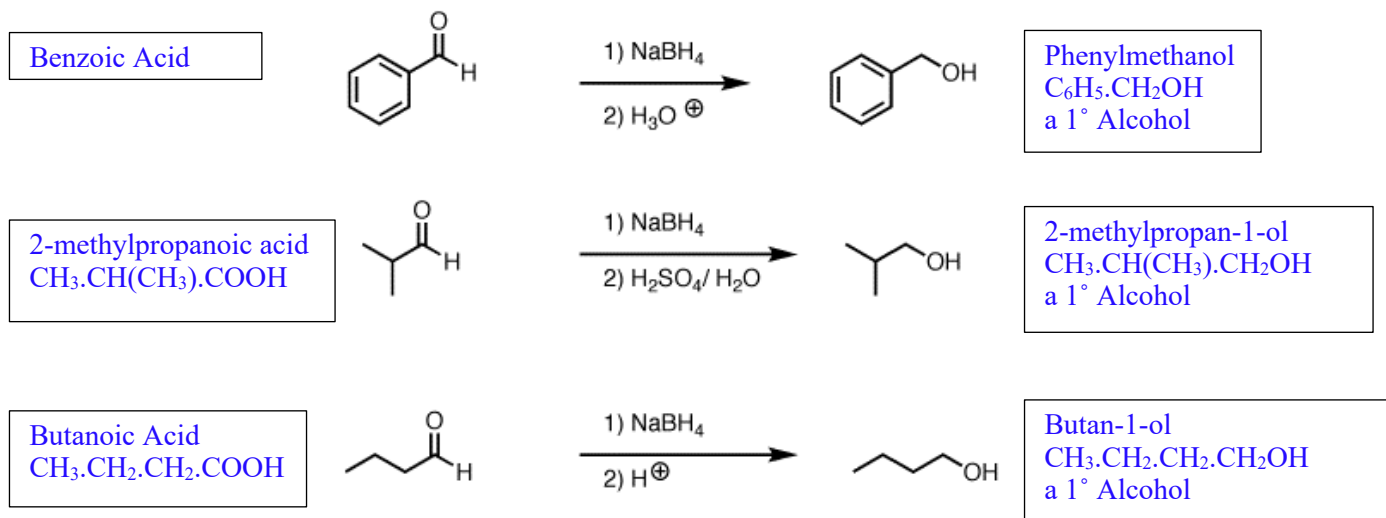


The **Nucleophilic Addition** reaction of an Aldehyde with Hydrogen Cyanide (HCN) will create a Nitrile – and for Organic Synthesis it is sensible to know that Nitriles can be reacted (with *dilute* Hydrochloric acid) to form the appropriate Carboxylic Acid. (“H<sup>+</sup> and Water” signifies a dilute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

**The Reduction of an Ketone into a 2° Alcohol**

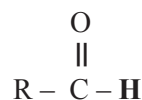
In the First Year we saw how a 1° Alcohol was oxidised into an Aldehyde, and now we can see how to reverse the process and reduce an Aldehyde into a 1° Alcohol (and a Ketone would correspondingly be reduced to a 2° Alcohol). A Carboxylic Acid would of course be reduced first to an Aldehyde and then to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

The two main reducing agents here are Lithium Aluminium Hydride (LiAlH<sub>4</sub>) and Sodium BoroHydride (NaBH<sub>4</sub>). LiAlH<sub>4</sub> can exhibit violent reactions but it is a more powerful reducing agent than NaBH<sub>4</sub>. Dr James Ashenurst of “Master Organic Chemistry” shows some examples of the reduction thus.



I think that that is enough on Ketones, but let me sum it up.

### ALDEHYDE



### KETONE



Ketones resist gentle oxidation.

Under gentle oxidation with  $\text{K}_2\text{Cr}_2\text{O}_7$  and conc  $\text{H}_2\text{SO}_4$  Aldehydes are converted into Carboxylic Acids.

$\text{LiAlH}_4$  will reduce an Aldehyde to a  $1^\circ$  Alcohol, and a Ketone into a  $2^\circ$  alcohol.

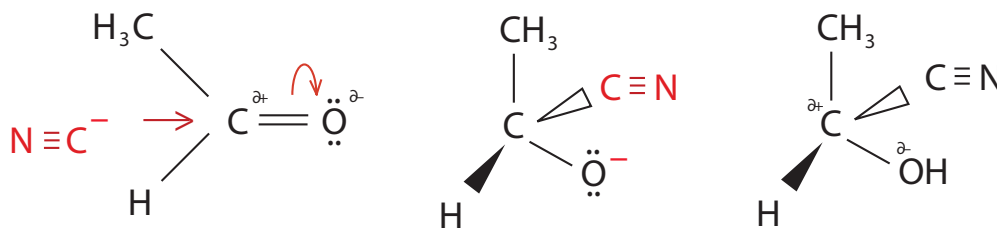
#### Test for an Aldehyde

It will react with Tollens (silver ppt),  
and with Fehling's or Benedict's  
(cyan  $\text{Cu}^{2+}$  goes reddy-brown because of  $\text{Cu}^+$  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 (" $\text{CN}^-$ ") species then a Nitrile is formed.



### Conversion of the Nitrile into a Carboxylic Acid

