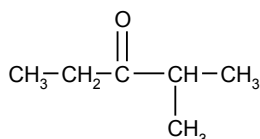


Carbonyl Chemistry

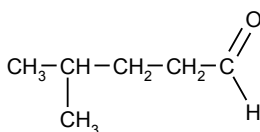
Carbonyl compounds are those which contain $>C=O$

- aldehydes
- ketones
- carboxylic acids
- esters

You should recall how to name aldehydes and ketones:

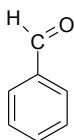


- longest chain is 5 carbons, so "-pentan-" stem
 - ketones have "-one" ending
 - C=O is located on 3rd carbon in chain
 - has a methyl group
 - methyl group on 2nd carbon (numbering for smallest)
- 2-methylpentan-3-one**



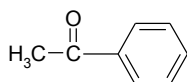
- longest chain is 5 carbons so "-pentan-" stem
 - aldehydes have an "-al" ending
 - numbering starts from the end with the aldehyde
 - methyl group is therefore on 4th carbon
- 4-methylpentanal**

The simplest aromatic aldehyde and ketone are:



benzaldehyde

- colourless liquid (at RT) with almond-like aroma
- almond essence, gives flavour to marzipan



phenylethanone

- used to create fragrances which resemble cherry, strawberry, honeysuckle or jasmine

Chemical tests to distinguish carbonyl compounds

1: Detecting an aldehyde or ketone

Aldehydes and ketones react with 2,4-dinitrophenylhydrazine (2,4-DNP or 2,4-DNPH) to form an orange or yellow precipitate. No precipitate is formed with other carbonyl compounds such as carboxylic acids or esters. *Brady's Reagent is a solution of 2,4-DNPH in methanol and sulphuric acid.*

A few drops of the carbonyl compound are put in a test tube with about 5cm³ of Brady's reagent. The precipitate formed, referred to as a 2,4-dinitrophenylhydrazone derivative, can be used to help identify the specific aldehyde or ketone, after purifying, by

measuring its melting point. This works well because the different derivatives have melting points that are many degrees apart.

e.g.

heptan-2-one	b.p. = 151°C	m.p of 2,4-DNP derivative	= 90°C
cyclohexanone	b.p. = 156°C	m.p of 2,4-DNP derivative	= 162°C
octan-2-one	b.p. = 173°C	m.p of 2,4-DNP derivative	= 58°C

Identifying an aldehyde/ketone from the 2,4-DNPH derivative:

- The orange/yellow solid substance is purified by recrystallisation
- Melting point is determined
- Melting point is compared to a database of published melting points for these derivatives

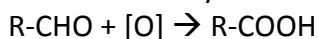
You will not be asked to write an equation for the formation of a 2,4-DNP derivative or to recall who to draw the structure of a 2,4-dinitrophenylhydrazone derivative.

2: Telling an aldehyde from a ketone

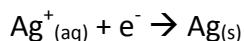
A further test is necessary to distinguish an aldehyde from a ketone. Aldehydes can be further oxidised to carboxylic acids, but ketones cannot.

Tollens' reagent is a weak oxidising agent containing **silver nitrate in ammonia**. Aldehydes can be oxidised further whereas ketones are not oxidised. The oxidising agent is the aqueous silver (I) ion, $\text{Ag}^+_{(\text{aq})}$. When warmed with Tollens reagent, the aldehyde is **oxidised to a carboxylic acid**, and the silver ions in solution are **reduced to silver metal**. A "silver mirror" is formed on the walls of the test tube (or sometimes just a silver-grey solid is formed).

Oxidation of the aldehyde:



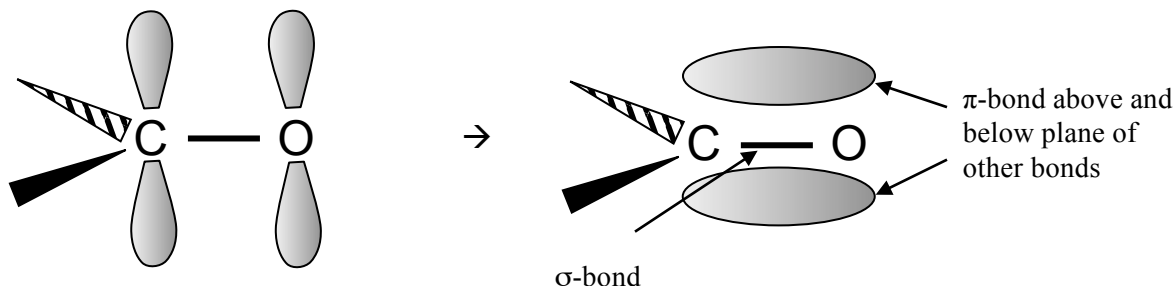
Reduction of the silver ions:



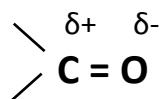
How the carbonyl group reacts

Firstly we need to understand a little more about the carbonyl group:

1. Like a C=C double bond, it is comprised of a sigma bond and a pi bond formed by the overlap of p-orbitals on the C and O atoms.



2. Unlike a C=C double bond, the C=O bond has a dipole. The electrons in the sigma and pi bonds are more attracted to the O than the C. This is because oxygen is much more electronegative than carbon. As a result the C is $\delta+$ and the O is $\delta-$.



Because of this difference the reactions of C=O are different to those of C=C; it is attacked by different reagents.

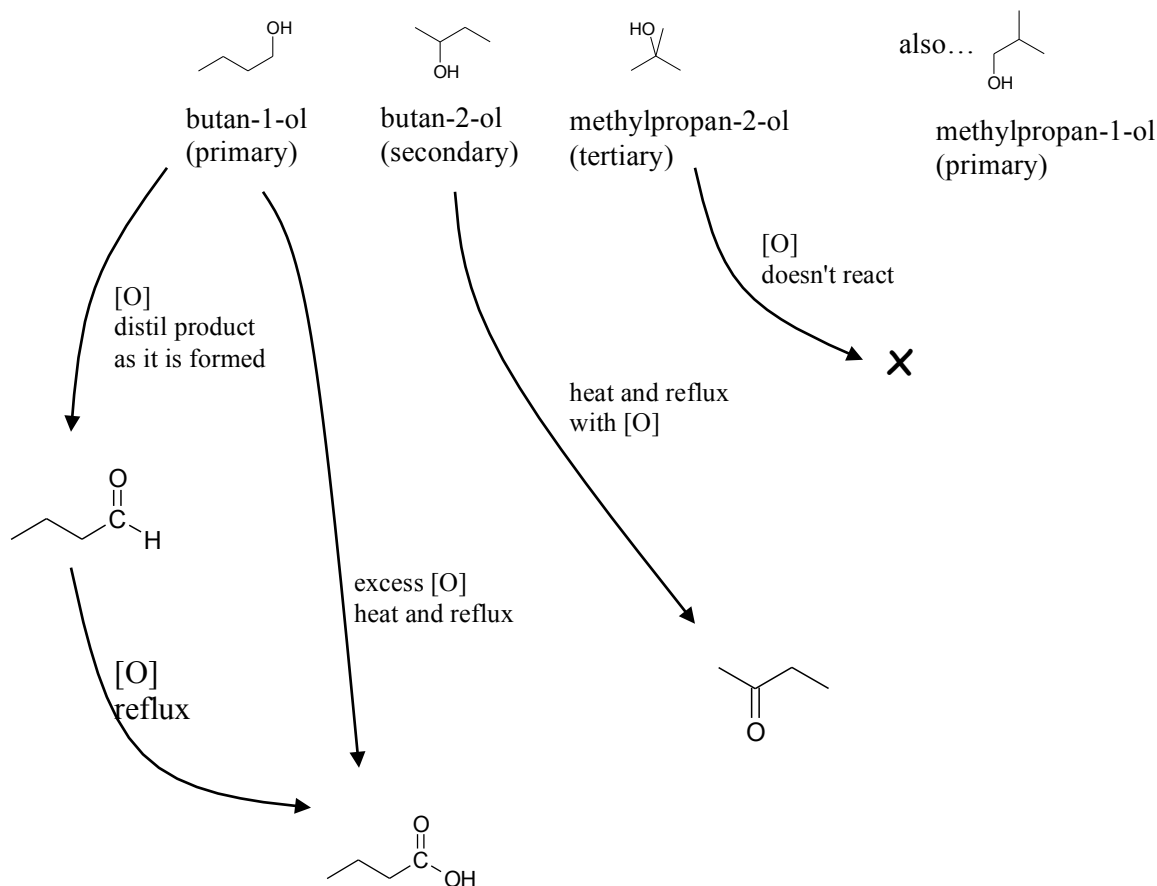
Oxidation Reactions

Recall that alcohols can be oxidized to form aldehydes, ketones and carboxylic acids.

The product depends on:

- which alcohol you use (primary or secondary – tertiary alcohols don't react)
- the reaction conditions

Consider the isomers of butanol – this example gives us primary, secondary and tertiary alcohols. The oxidising agent is here represented by [O].



Reagent:

A suitable reagent is a solution of $\text{NaBH}_{4(\text{aq})}$, sodium borohydride (sodium tetrahydridoborate III). This is a source of hydride ions, H^- , which are the actual reducing agent. We can represent these in equations by $[\text{H}]$.

Conditions:

- Usually carried out by **warming** the carbonyl compound with the reducing agent.
- Water is used as the solvent.

Equations:

- use $[\text{H}]$ for the reducing agent
- never write as ambiguous molecular formulae: structural, displayed or skeletal!

Aldehydes are reduced to primary alcohols, e.g. $\text{CH}_3\text{CH}_2\text{CHO} + 2[\text{H}] \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

Ketones are reduced to secondary alcohols, e.g. $\text{CH}_3\text{COCH}_3 + 2[\text{H}] \rightarrow \text{CH}_3\text{CH}_2(\text{OH})\text{CH}_3$

Mechanism of nucleophilic addition:

The H^- ion is a hydrogen atom with an extra electron in its shell, meaning it has a lone pair, and is negatively charged. It can donate this lone pair to form a bond, so it is a nucleophile. Nucleophiles attack δ^+ centres – in this case the δ^+ carbon of the $\text{C}=\text{O}$.

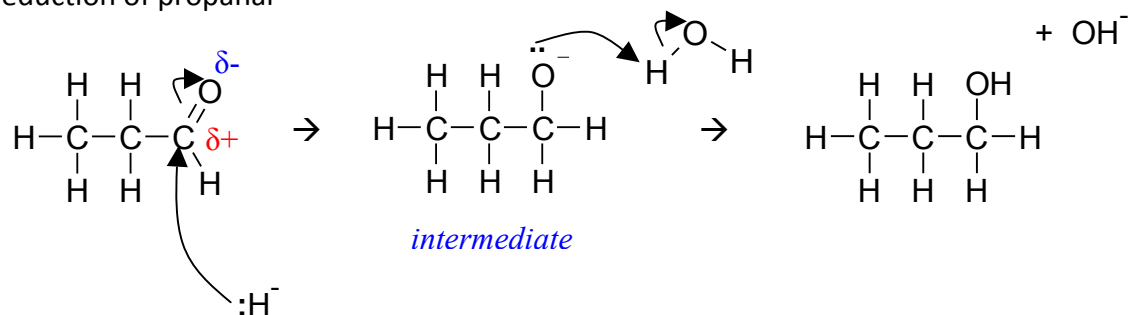
In the first stage

- the hydride ion attacks the δ^+ carbon, using its lone pair to form a new bond.
- the pi-bond between C and O atoms breaks, leaving an intermediate $\text{C}-\text{O}^-$ with a single bond and a negative charge on the O atom.

In the second stage

- the O atom of the intermediate donates a lone pair to a hydrogen atom of a water molecule forming a dative bond.
- the O-H bond in water breaks heterolytically leaving hydroxide ion.

e.g. reduction of propanal



Don't represent the second stage as O^- : forming a bond to an H^+ ion – there aren't H^+ ions available, this isn't done under acidic conditions, unlike with NaCN/H^+ when there are, and H^+ can be used.

ii) reaction with HCN to form hydroxynitriles

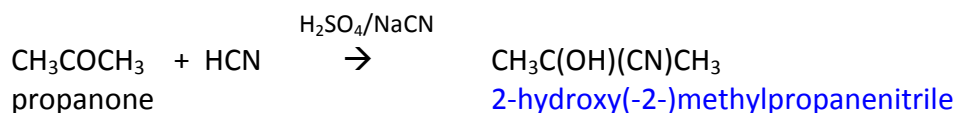
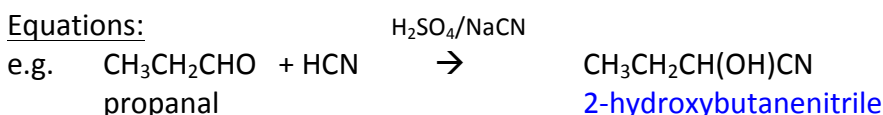
Hydrogen cyanide adds across the C=O to produce an –OH group and add a –CN (nitrile) group to the molecule. This is very useful in synthesis as it extends the carbon skeleton.

Reagent:

Hydrogen cyanide is colourless, extremely poisonous, and volatile boiling just above room temperature – it cannot be used safely in the laboratory so sodium cyanide and sulphuric acid are used to produce HCN in-situ. The reaction is still very hazardous.

Conditions:

Not required.

Equations:Mechanism of nucleophilic addition:

The initial attack on the δ^+ carbon of the C=O is by the cyanide ion, often written as CN^- . This is a little misleading, as the negative charge is on the carbon atom, and it is a lone pair on the carbon that attacks. It is better to represent as $[\text{:CN}]^-$ or ^-CN .

In the first stage

- the ^-CN ion attacks the δ^+ carbon, using its lone pair to form a new bond.
- the pi-bond between C and O atoms breaks, leaving an intermediate C-O^- .

In the second stage

- the O atom of the intermediate donates a lone pair to a hydrogen atom of a water molecule forming a dative bond (*or an H^+ ion in solution, OK for this reaction*)
- the O-H bond in water breaks heterolytically leaving hydroxide ion.

