Organic chemistry – crib sheet

Aldehydes and ketones

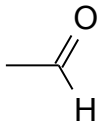
General

Aldehydes and ketones are a group of carbonyl compounds containing a double bonded O to a carbon. There are some key differences though

Aldehydes are terminal compounds (they occur at the end of the chain only) whereas a **ketone** can only occur in the middle of a chain or where there is a carbon on either side of the carbon bonded to the oxygen,.

Structure and bonding

Aldehydes are terminal compounds consisting of a double bonded oxygen and a single bonded H (*right*). The reactivity of the compound comes from the negative charge on the oxygen.

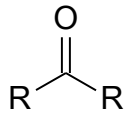


Aldehydes are capable of hydrogen bonding with themselves and with water, so the melting and boiling points are fairly high (except for methanal, all aldehydes are liquid at room temperature). Aldehydes are also by-products of bacterial breakdown or oxidation of skin oils (they leave a slightly acrid smell). In the human body, enzymes break down alcohol molecules taken in, to ethanal, which the body can then remove

Aldehydes will undergo oxidation reactions to form carboxylic acids due to the removable hydrogen on the terminal carbon.

As aldehydes are terminal compounds, they are one of the few functional groups which change the name of the alcohol group to hydroxy. The numbering of other groups also starts from here.

Ketones (*right*) have a double bonded carbon, but this time requires two carbon containing groups on either side (R = any carbon containing group).

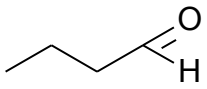


Due to there being no hydrogens present, hydrogen bonding with itself is not possible but is possible with water. As a carbon is needed on either side of the double bonded oxygen, the smallest ketone possible is propanone.

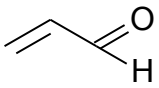
Aldehydes are produced by the oxidation of 1º alcohols and ketones from the oxidation of 2º alcohols

Naming aldehydes

1. As with all carbon containing compounds, the skeletal part of the name comes from the longest unbroken carbon chain.
2. Find any other groups. The terminal carbon is counted as 1. If there are two aldehydes on the chain, the branch nearest to aldehyde is given the lowest number.
3. Add -al to the end of the skeletal name
4. As with other compounds, name the branches in number order, the skeletal name and then ending



Longest chain : 4 carbons = butan
Functional group : aldehyde, ends in -al
Any other branches : no
Full name : butanal

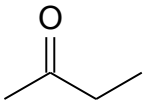


Longest chain : 3 carbons = prop
Functional group : aldehyde, ends in al
Any other groups : yes, double bond on C2
Full name : propenal

Note : In this example, the number for the double bond is not required. It would not be possible to have the double bond on C1-C2 as this would make C1 have 5 bonds.

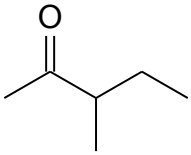
Naming ketones

1. Find the longest carbon chain.
2. The C=O can be almost anywhere on a chain, it needs to be given a number. As with other branches, it has a priority which is based on atomic weight (O > CH_3 but less than F).
3. The ending for a ketone is -one
4. The full name is written as groups-skeletal name-one



Longest chain : 4 carbons = butan
Functional group : ketone, ends in -one
Other branches : No
Full name : butan-2-one (or 2-butanone)

Note : In this example, the 2 can be safely left out. Remember a ketone has to have a carbon on either side of the C=O. As there are 4 carbons in this chain with no multiple bonds, saying 3-butanone would be incorrect as this would be a mirror image of 2-butanone.



Longest chain : 5 carbons = pentan
Functional group : ketone, ends in -one
Other branches : Yes, methyl
Priority : O > CH3, therefore ketone on 2 carbon, methyl on 3
Full name : 3-methyl pentan-2-one (or 3-methyl pentanone)

Note : In this example, as the methyl is in the middle, the position of the C=O is 2. In the same way as for the 1st example, saying pentan-4-one is incorrect as this is the same as pentan-2-one – they are mirror images.

Reactions of aldehydes

Aldehydes can be oxidised to carboxylic acids or reduced back to alcohols.

Oxidation reactions of aldehydes

Oxidation reactions do not require strong oxidation conditions, the use of Fehlings or Benedicts reagents (both containing Cu^{2+} ions), Tollens solution (Ag^{+}) or acidified potassium dichromate (Cr^{6+}) are commonly used.

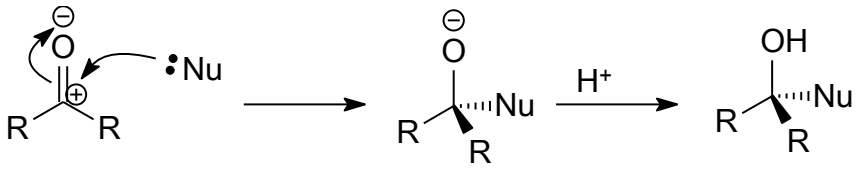
Oxidising agent	Reaction	Results
Fehlings Benedicts	$Cu^{2+} + e \rightarrow Cu^{+}$	Blue solution forms an orange solid in the bottom
Tollens	$Ag^{+} + e \rightarrow Ag$	A silver mirror is left on the reaction vessel
$K_2Cr_2O_7$	$Cr^{6+} + 3e \rightarrow Cr^{3+}$	Solution goes from orange to blue/green

The oxidation of an aldehyde gives the corresponding carboxylic acid (e.g. ethanal → ethanoic acid)

Reactions of aldehydes and ketones

Due to the charge on the C=O, both aldehydes and ketones can undergo nucleophilic addition reactions. This is a 2 stage process

Step 1 is the attack of the nucleophile on the δ+ carbon atom to leave a negatively charged oxonium ion.
Step 2 is the addition of a proton to the oxonium to give the alcohol.

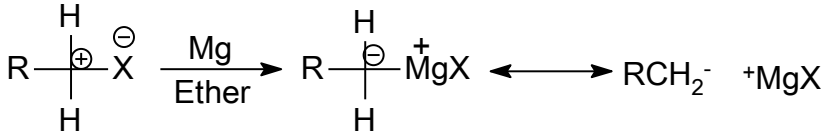


This is a very handy method of adding the likes of nitrile (-C≡N) and amine ($-NH_2$) containing groups to a chain.

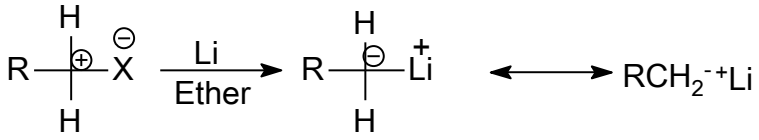
A more important form of reaction involving aldehydes and ketones is those involving organometallic compounds (such as organolithium [R-Li] and Grignard reagents [R-Mg-X where X is a halide]). These will result in the production of alcohols.

Addition using organometallic compounds

1. Grignard reagent. Here X is Br or I.



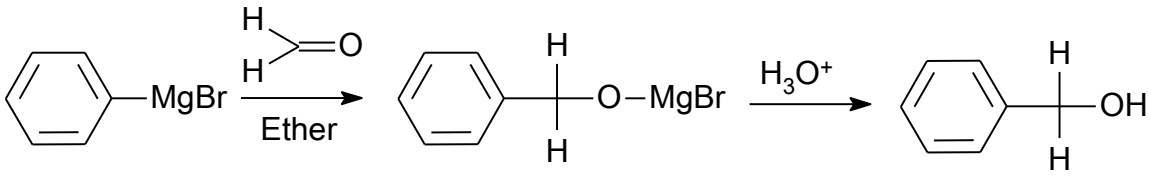
2. Organolithium. Here X is Br or I.



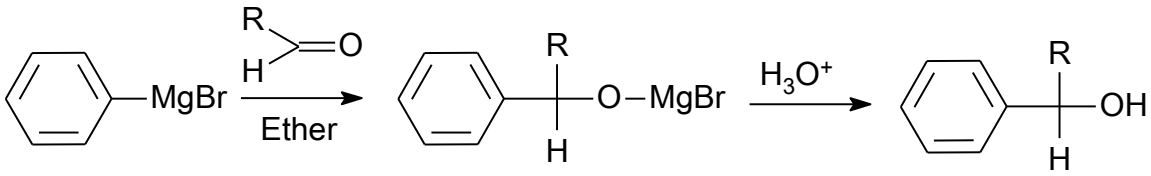
Note in both cases that the carbon alters charge from positive to negative (the Mg and Li are both stronger electrophiles than the carbons). Note also that for the initial step, the reaction has to be performed in ANHYDROUS (no water) conditions.. Water destabilises the Grignard and organolithium compounds

Grignard reaction with aldehydes

The reaction with methanal using a Grignard reagent results in a primary alcohol being produced

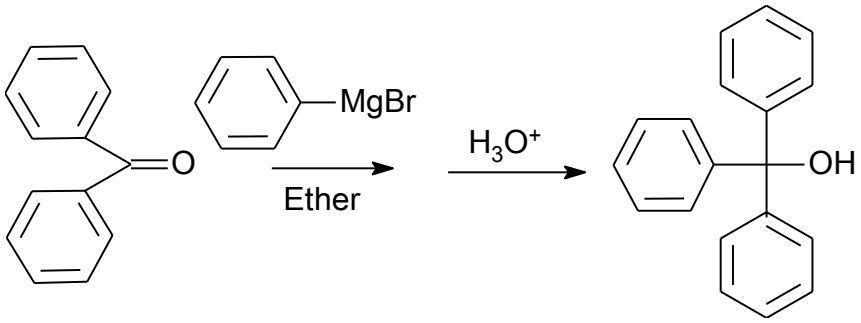


The reaction between any other aldehyde and a Grignard reagent results in a 2º alcohol



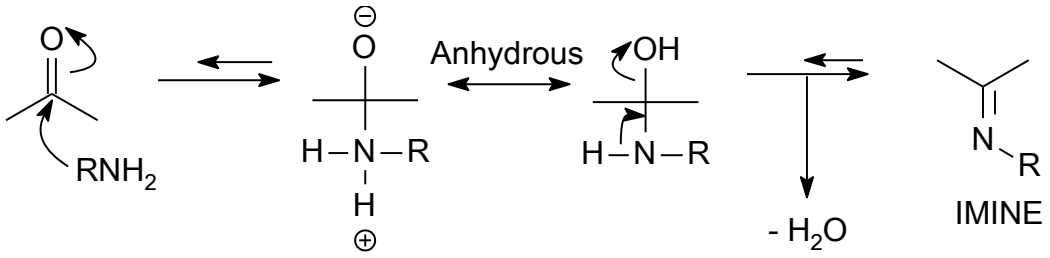
Grignard reaction with ketones

Ketones react with Grignard reagents to form 3º alcohols



Addition of amines

Amines are strong nucleophiles and will readily react with aldehydes and ketones to form imines

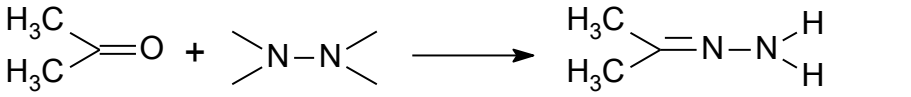


Imines have a reactive C=N bond which will also undergo further reactions by electrophiles.

Production of hydrazines

Hydrazines are a group of compounds that form crystalline compounds when they react with either aldehydes or ketones. They are typically used as compounds used in the production of dyes and drugs.

Hydrazine is capable of reacting with either aldehydes or ketones to produce hydrazones with the elimination of water



propanone hydrazine hydrazone of propanone