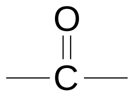
م.م زينب يحيى كاظم

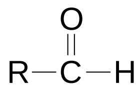
ALDEHYDES AND KETONES

The major similarity between an aldehyde and a ketone is the carbonyl group. A carbonyl group is a carbon atom doubly bonded to an oxygen atom.

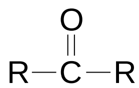


Both molecules have a carbonyl group, the difference the number of carbons bonded to the carbonyl carbon. An aldehyde will have none or one and a ketone will have two carbons.

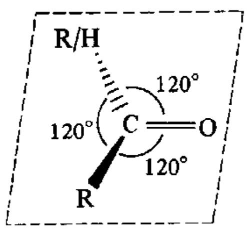
All aldehydes, except formaldehyde, will have a hydrogen atom on one side of the carbonyl carbon and at least on carbon on the other side.



All ketones have a carbon on each side of the carbonyl carbon.



The carbonyl carbon is sp^2 hybridised, with its three attached atoms lying in the same plane. The bond angles between the three attached atoms are what is expected for a trigonal planar structure: approximately 120^0.



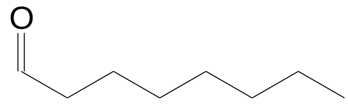
Nomenclature:

Aldehydes – IUPAC Names

1. Count the number of carbons in the longest chain containing the aldehyde group

2. The carbonyl carbon will always be carbon number one
3. Drop the –e suffix and add –al

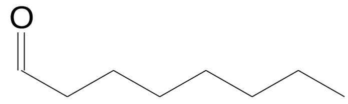
Examples:

$CH_3-C(=O)-H$	$CH_3CH_2-C(=O)-H$	$CH_3CH_2CH_2-C(=O)-H$	
ethanal	propanal	butanal	octanal

Aldehydes – Common Names

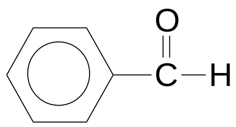
1. Count the number of carbons
2. Use the side-chain abbreviation
3. Add the word aldehyde to the end

Examples:

$CH_3-C(=O)-H$	$CH_3CH_2-C(=O)-H$	$CH_3CH_2CH_2-C(=O)-H$	
ethyl aldehyde	propyl aldehyde	butyl aldehyde	octyl aldehyde

Aldehydes – Very Common Names

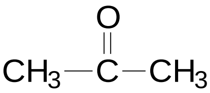
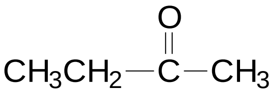
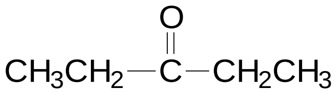
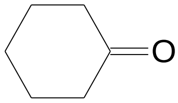
Just as H_2O is referred to as water some aldehydes have very common names. The following is a list of these very specific common names.

$H-C(=O)-H$	$CH_3-C(=O)-H$	
formaldehyde	acetaldehyde	benzaldehyde

Ketones – IUPAC Names

1. Count the number of carbons in the longest chain containing the ketone group
2. The carbonyl carbon will always be given the lowest possible number
3. Drop the –e suffix and add –one

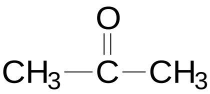
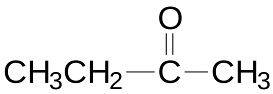
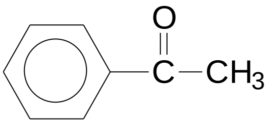
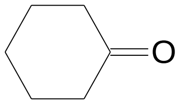
Examples:

			
propanone	butanone	3-pentanone	cyclohexanone

Ketones – Common Names

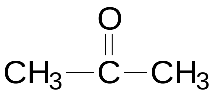
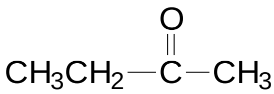
1. Count the number of carbons
2. Use the side-chain abbreviation
3. Add the word ketone to the end

Examples:

			
dimethyl ketone	methyl ethyl ketone	methyl phenyl ketone	cyclohexanone

Ketones – Very Common Names

Just as H_2O is referred to as water some ketones have very common names. The following is a list of these very specific common names.

	
acetone	MEK

Bonding and reactivity

Bonding in the carbonyl group

Oxygen is far more electronegative than carbon and so has a strong tendency to pull electrons in a carbon-oxygen bond towards itself. One of the two pairs of electrons that make up a carbon-oxygen double bond is even more easily pulled towards the oxygen. That makes the carbon-oxygen double bond very highly polar.

Important reactions of the carbonyl group

The slightly positive carbon atom in the carbonyl group can be attacked by ***nucleophiles***. A nucleophile is a negatively charged ion (for example, a cyanide ion, CN^-), or a slightly negatively charged part of a molecule (for example, the lone pair on a nitrogen atom in ammonia, NH_3). During the reaction, the carbon-oxygen double bond gets broken. The net effect of all this is that the carbonyl group undergoes ***addition reactions***, often followed by the loss of a water molecule. This gives a reaction known as ***addition-elimination*** or ***condensation***

Where aldehydes and ketones differ

An aldehyde differs from a ketone by having a hydrogen atom attached to the carbonyl group. This makes the aldehydes very easy to oxidizes. For example, ethanal, CH_3CHO, is very easily oxidized to either ethanoic acid, CH_3COOH, or ethanoate ions, CH_3COO^-. Ketones don't have that hydrogen atom and are resistant to oxidation. They are only oxidised by powerful oxidising agents which have the ability to break carbon-carbon bonds.

Physical properties

Boiling points

Methanal is a gas (boiling point -21°C), and ethanal has a boiling point of +21°C. That means that ethanal boils at close to room temperature. The other aldehydes and the ketones are liquids, with boiling points rising as the molecules get bigger. The size of the boiling point is governed by the strengths of the intermolecular forces.

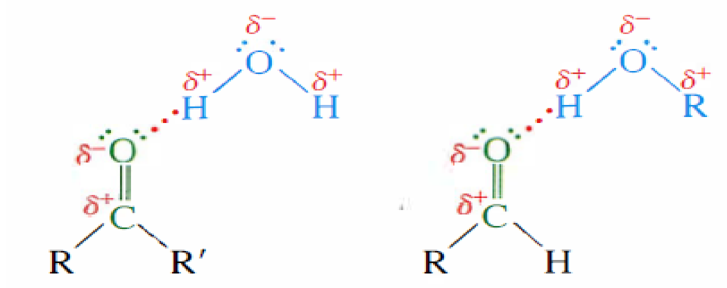
Boiling point:

- ❖ Aldehydes and ketones are **polar compounds** due to the **polarity of carbonyl group** and hence they have **higher boiling points** than **nonpolar compounds** of comparable molecular weight.

- **But** they have **lower boiling points** than comparable **alcohols or carboxylic acids** due to the **intermolecular hydrogen bonding**.

Solubility in water

The **lower** aldehydes and ketones solubility **in water**, because of **hydrogen bonding between carbonyl group and water**, also they solubility **in organic solvents.** Low-molecular weight aldehydes and ketones are **water-** solubility**;** water solubility decreases as the size of the molecule increases.



Boiling Points:

↑ Alcohols
Aldehydes/Ketones
Ethers
Alkanes

Water Solubility:

↑ Alcohols
Aldehydes/Ketones
Ethers
Alkanes

Name	Molecular weight	Boiling point	Solubility in water
butane	58 g/mol	0°C	Insoluble
propanal	58 g/mol	49°C	Soluble
acetone	58 g/mol	56°C	Soluble
1-propanol	60 g/mol	97°C	Soluble

Examples: Predicting Boiling Points

- Arrange the following compounds in order of increasing boiling point:
  - – 2-pentanone
  - – 2-methylpentane
  - – 2-pentanol

Type of Compound	Compound	Structure	Molecular Mass	Boiling Point (8°C)
alkane	ethane	$CH_3—CH_3$	30	−89
aldehyde	methanal	H—CHO	30	−21
alcohol	methanol	$CH_3—OH$	32	65
alkane	propane	$CH_3—CH_2—CH_3$	44	−42
aldehyde	ethanal	$CH_3—CHO$	44	20
alcohol	ethanol	$CH_3—CH_2—OH$	46	78
alkane	butane	$CH_3—CH_2—CH_2—CH_3$	58	−1
aldehyde	propanal	$CH_3—CH_2—CHO$	58	49
alcohol	1-propanol	$CH_3—CH_3—CH_2—OH$	60	97

SIMPLE METHODS OF FORMATION OF ALDEHYDES AND KETONES

A. Preparation of Aldehydes

1. Oxidation of Primary Alcohols

Aldehydes may be prepared by the controlled oxidation of primary alcohols, using an acidified solution of potassium dichromate or potassium permanganate:

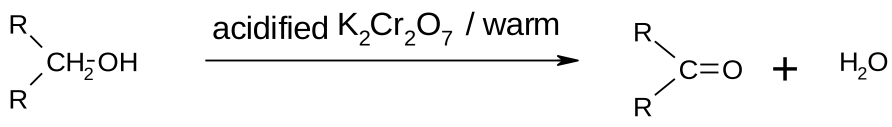
$$R\text{-}CH_2\text{-}OH \xrightarrow{\text{acidified } K_2Cr_2O_7 \text{ / warm}} RCHO + H_2O$$

The alcohol is added drop wise to the oxidising solution and the reaction mixture is kept at a temperature below the boiling point of alcohol but above that of the aldehyde. This allows the aldehyde formed to be distilled from the reaction mixture once it is formed, and avoids its further oxidation to carboxylic acid.

B. Preparation of Ketones

1. Oxidation of Secondary Alcohols ($KMnO_4$, $K_2Cr_2O_7$, [O])

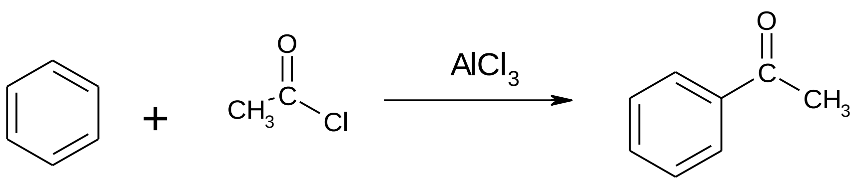
Ketones can also be obtained from oxidation of secondary alcohols, most commonly by the use of an acidified solution of dichromate:



The ketones formed in the reaction mixture can be similarly distilled out as it is formed, since carbonyl compounds are relatively volatile (no hydrogen bonding) and a good separation is easily obtained.

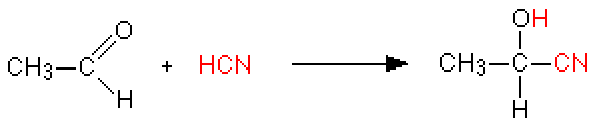
2. Friedal-Crafts Acylation

Many aromatic compounds react with acid chlorides in the presence of aluminium trichloride to give aromatic ketones. This Friedal-Crafts acylation has been discussed in chapter 11.

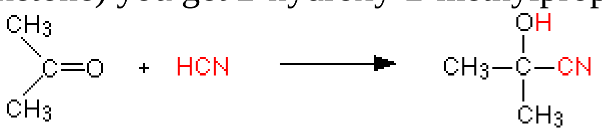


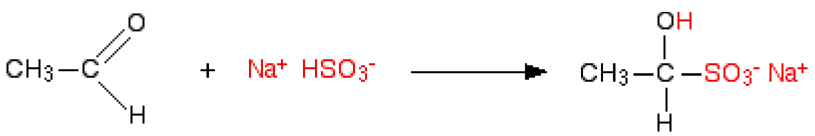
The reaction of aldehydes and ketones with hydrogen cyanide

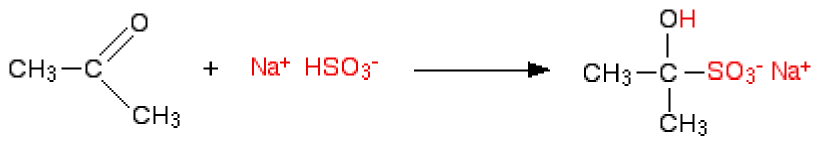
For example, with ethanal (an aldehyde) you get 2-hydroxypropanenitrile:



With propanone (a ketone) you get 2-hydroxy-2-methylpropanenitrile:







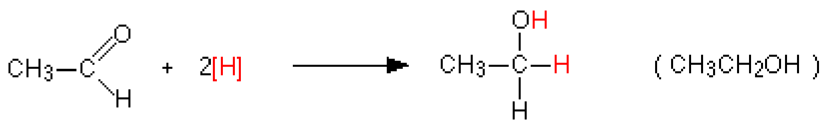
reduction of aldehydes and ketones

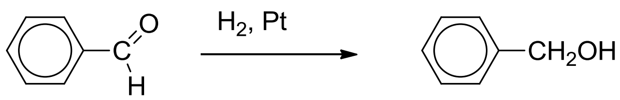
The formulae of the two compounds are $LiAlH_4$ and $NaBH_4$.

The reduction of an aldehyde

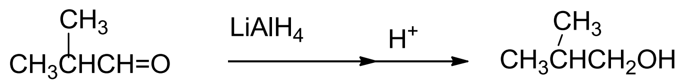
You get exactly the same organic product whether you use lithium tetrahydridoaluminate or sodium tetrahydridoborate.

For example, with ethanal you get ethanol:





benzaldehyde benzyl alcohol

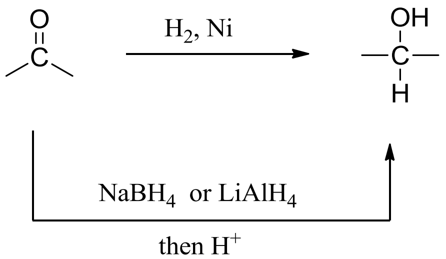


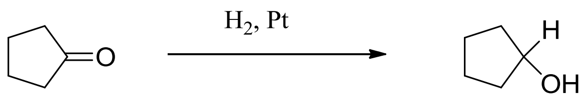
isobutyraldehyde isobutyl alcohol

In general terms, reduction of an aldehyde leads to a ***primary alcohol***.

The reduction of a ketone

Again the product is the same whichever of the two reducing agents you use. For example, with propanone you get propan-2-ol:





cyclopentanone cyclopentanol

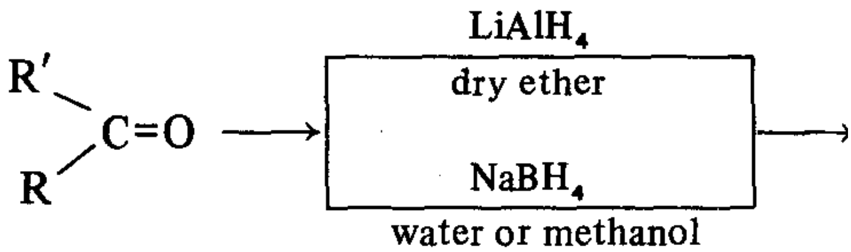
Reduction of a ketone leads to a ***secondary alcohol***.

Tollens' reagent:

Preparing by add NaOH to $AgNO_3$ (aq) to precipitate Ag_2O, then add ammonia to form the silver-ammonia complex ion. Tollens' reagent is specific for the oxidation of aldehydes. If silver deposits on the walls of the container as a silver mirror when Tollens' reagent is mixed with an unknown substance, the substance must be an aldehyde.

$$RCHO + 2Ag(NH_3)_2^+ \xrightarrow{NH_3,\ H_2O} RCOO^- + 2Ag + 4NH_3$$

Precipitates as silver mirror



1. Draw structures for the following compounds.

(a) 5-oxohexanal

(b) 3-methyl-3-buten-2-one

(c) isopropyl methyl ketone