

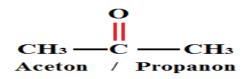
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Aldehydes and Ketones

Introduction :-

Aldehydes are defined as unsaturated organic compounds that contain terminal carbonyl groups.

Whereas, ketones are defined as unsaturated organic compounds that contain an intermediate or non-terminal carbonyl group.



Generally, the common names of ketones consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. (Note the similarity to the naming of ethers.) Another name for acetone, then, is *dimethyl ketone*. The ketone with four carbon atoms is ethyl methyl ketone.

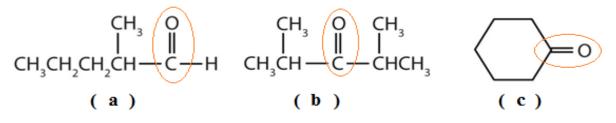


IUPAC rules for naming aldehydes and ketones:

- **1.** The stem names of aldehydes and ketones are derived from those of the parent alkanes, defined by the longest continuous chain (LCC) of carbon atoms that contains the functional group.
- 2. For an aldehyde, drop the *-e* from the alkane name and add the ending *-al*. Methanal is the IUPAC name for formaldehyde, and ethanal is the name for acetaldehyde.
- 3. For a ketone, drop the *-e* from the alkane name and add the ending *-one*. Propanone is the IUPAC name for acetone, and butanone is the name for ethyl methyl ketone.

- 4. To indicate the position of a substituent on an aldehyde, the carbonyl carbon atom is always considered to be C1; it is unnecessary to designate this group by number.
- 5. To indicate the position of a substituent on a ketone, number the chain in the manner that gives the carbonyl carbon atom the lowest possible number. In cyclic ketones, it is understood that the carbonyl carbon atom is C1.

Example:- Give the IUPAC name for each compound.



Solution

a. 1)-There are five carbon atoms in the long carbon chain .

2)-The methyl group (CH₃) is a substituent on the second carbon atom of the chain.

- 3)- The aldehyde carbon atom is always C1.
- 4)- The name is derived from pentane. Dropping the *-e* and adding the ending *-al* gives pentanal.
- 5)-The methyl group on the second carbon atom makes the name

2-methylpentanal.

b. 1)-There are five carbon atoms in the long carbon chain .

2)- The carbonyl carbon atom is C3, and there methyl groups on C2 and C4.

- 3)-The IUPAC name is 2,4-dimethyl-3-pentanone.
- c. 1)-There are six carbon atoms in the ring.

2)-The compound is cyclohexanone. No number is needed to indicate the position of the carbonyl group because all six carbon atoms are equivalent.

Example :- Draw the structure for each compound. A)-7-Chlorooctanal B)- 4-Methyl–3-hexanone

Solution A)-

1)- The *octan*- part of the name tells us that the long carbon chain has eight carbon atoms. 2)-There is a

chlorine (Cl) atom on the seventh carbon atom; numbering from the carbonyl group and counting the carbonyl carbon atom as C1, we place the Cl atom on the seventh carbon atom.

B)- 1)- The *hexan*- part of the name tells us that the long carbon chain has six carbon atoms.

2)- The 3 means that the carbonyl carbon atom is C3 in this chain, and the 4 tells us that there is a methyl (CH₃) group at C4:



Example_ Draw the structure for each compound. A)-Butanal b)- 2-hexanone

Solution

$$\begin{array}{c} \mathbf{CH}_{3}\mathbf{CH}_{2}\mathbf{CH}_{2}\mathbf{CH}\mathbf{O} \\ \mathbf{II} \\ \mathbf{CH}_{3}\mathbf{--CH}_{2}\mathbf{CH}_{2}\mathbf{CH}_{2}\mathbf{CH}_{2}\mathbf{CH}_{2}\mathbf{CH}_{2}\mathbf{CH}_{3} \\ \text{(a)} \\ (b) \end{array}$$

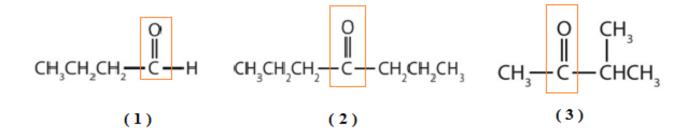
Where aldehydes and ketones different

An aldehyde differents from a ketone by having a hydrogen atom attached to the carbonyl group.

This makes the aldehydes very easy to oxidize. For example, ethanal, CH₃CHO, is very easily oxidised to either ethanoic acid, CH₃COOH, or ethanoate ions, CH₃COO⁻¹

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

Example :- Classify each compound as an aldehyde or a ketone. Give the common name for each ketone .



Solution

1. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde.

- 2. This compound has the carbonyl group on an interior carbon atom, so it is a ketone. Both alkyl groups are propyl groups. The name is therefore dipropyl ketone.
- 3. This compound has the carbonyl group between two alkyl groups, so it is a ketone. One alkyl group has three carbon atoms and is attached by the middle carbon atom; it is an isopropyl group. A group with one carbon atom is a methyl group. The name is therefore isopropyl methyl ketone.

Preparation of Aldehydes and Ketones

<u>1-Oxidation of alcohols: -</u>

We have already studied in alcohols and phenols that <u>oxidation of alcohols</u> converts primary and secondary alcohols to aldehydes and ketones by used Collins reagents (Chromium trioxide-pyridine complex) (Reagent

A). Primary alcohols

CH₃CH₂-OH (Reagent A) or Cu at 573K CH₃CHO

B)Secondary alcohols

$$\frac{(\text{Reagent A})}{\text{or Cu at 573K}} \xrightarrow{\text{CH}_3\text{C}(=0)} \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$$

<u>2- Ozonolysis of alkenes</u>

Alkenes react with O₃ in the presence of Zn and H₂O to produce aldehydes or ketones depending upon the structure of alkene.

<u>3-From hydration of alkynes</u>

Alkynes undergo hydration according to <u>Markovnikov's rule</u> in the presence of catalyst HgSO₄ and H₂O to give ketones.

 $CH_3-C \equiv CH + H_2O \xrightarrow{H_2SO_4} CH_3- \xrightarrow{C} = CH_2 \xrightarrow{rearrangement} CH_3- \xrightarrow{O} CH_3- \xrightarrow{O} CH_3$

Note :- Ethyne gives aldehyde instead of ketones

 $CH \equiv CH + H_2O \longrightarrow CH_3 - CHO$

4-Preparation of ketones

Treatment of acid chloride with dialkylcadmium [(R)₂Cd] gives ketones.

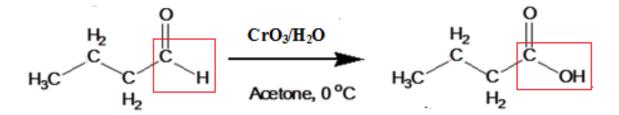
 $2R-COC1 + (R')_2 Cd \longrightarrow 2RCOR' + CdCl_2$

 $2 (CH_3) CO Cl + (CH_3CH_2)_2Cd \rightarrow 2 CH_3COCH_2CH_3 + CdCl_2$

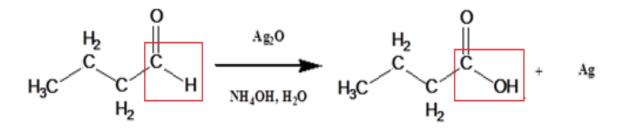
Reaction Of Aldehydes and Ketons

1-Oxidation of Aldehydes and ketones:-

The presence of that hydrogen atom makes aldehydes very easy to oxidize . The most common reagent for this conversion is CrO₃ in aqueous acid. This reaction generally gives good yields at room temperature.



The acid condition for the previous reaction can cause unwanted side reaction. If this problem occurs it can be rectified by using a solution of sliver oxide, Ag₂O in aqueous ammonia, also called Tollens' reagent.



2-Reduction Aldehydes and ketones

Aldehydes and ketones are most readily reduced by use the reducing agents $LiAlH_4$ and $NaBH_4$.Hydride reacts with the carbonyl group, C=O, in aldehydes or ketones to give alcohols. The reduction of other aldehydes gives primary alcohols and reduction of ketones gives secondary alcohols .this Reactions usually in Et_2O or THF followed by H_3O^+ .

