**Organic Chemistry** 

## **Aldehydes and Ketones**

Aldehydes are compounds of the general formula RCHO; ketones are compounds of the general formula RR'CO. The groups R and R' may be aliphatic or aromatic.



Both aldehydes and ketones contain the carbonyl group, C=O, and are often referred to collectively as carbonyl compounds. It is the carbonyl group that largely determines the chemistry of aldehydes and ketones.

It is not surprising to find that aldehydes and ketones resemble each other closely in most of their properties. However, there is a hydrogen atom attached to the carbonyl group of aldehydes, and there are two organic groups attached to the carbonyl group of ketones. This difference in structure affects their properties in two ways:

(a) aldehydes are quite easily oxidized, whereas ketones are oxidized only with difficulty.

(b) aldehydes are usually more reactive than ketones toward nucleophilic addition, the characteristic reaction of carbonyl compounds.

### Nomenclature

The common names of aldehydes are derived from the names of the corresponding carboxylic acids by replacing -ic acid by -aldehyde.

The IUPAC names of aldehydes follow the usual pattern. The longest chain carrying the -CHO group is considered the parent structure and is named by replacing the -e of the corresponding alkane by -al. The position of a substituent is indicated by a number, the carbonyl carbon always being considered as C-l.

Here, as with the carboxylic acids, we notice that C-2 of the IUPAC name corresponds to alpha of the common name.



The simplest aliphatic ketone has the common name of acetone. For most other aliphatic ketones we name the two groups that are attached to carbonyl carbon, and follow these names by the word ketone. A ketone in which the carbonyl group is attached to a benzene ring is named as a -phenone, as illustrated below.

According to the IUPAC system, the longest chain carrying the carbonyl group is considered the parent structure, and is named by replacing the -e of the corresponding alkane with -one. The positions of various groups are indicated by numbers, the carbonyl carbon being given the lowest possible number.

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Propanone

CH<sub>3</sub>CH<sub>2</sub>-C-CH<sub>3</sub>

Methyl ethyl ketone Butanone

CH3 CH<sub>3</sub> CH<sub>3</sub>CH

Methyl isopropyl ketone 3-Methyl-2-butanone

CH<sub>3</sub>

⊘−с−сн₂сӊ₂сӊ₃

Acetophenone

n-Butyrophenone

 $NO_2$ 

3-Nitro-4.'-methylbenzophenone

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-CH<sub>3</sub>

Methyl *n*-propyl ketone 2-Pentanone

СН₃

Benzyl methyl ketone 1-Phenyl-2-propanone

Benzophenone

## **Physical properties**

The polar carbonyl group makes aldehydes and ketones polar compounds, and hence they have higher Boiling points than non-polar compounds or comparable molecular weight. By themselves, they are not capable of intermolecular hydrogen bonding since they contain hydrogen bonded only to carbon; as a result they have lower boiling points than comparable alcohols or carboxylic acids.

The lower aldehydes and ketones are appreciably soluble in water, presumably because of hydrogen bonding between solute and solvent molecules; borderline solubility is reached at about five carbons. Aldehydes and ketones are soluble in the usual organic solvents.

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## **PREPARATION OF ALDEHYDES**

1. Oxidation of primary alcohols.



### Example:

 $\begin{array}{cccc} CH_{3}CH_{2}CH_{2}CH_{2}OH & \xrightarrow{K_{2}Cr_{2}O_{7}, H_{2}SO_{4}, warm} & CH_{3}CH_{2}CH_{2}CH_{2}CHO \\ \hline n-Butyl alcohol & & n-Butyraldehyde \\ (1-Butanol) & & & (Butanal) \end{array}$ 

2. Oxidation of methylbenzenes.



Examples:



3. Reduction of acid chlorides.

RCOCI or ArCOCI  $\xrightarrow{\text{LiAlH(Bu-1)_3}}$  RCHO or ArCHO Acid chloride Aldehyde

Examples:



4. Reimer-Tiemann reaction. Phenolic aldehydes.



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#### **PREPARATION OF KETONES**

1. Oxidation of secondary alcohols.



# **REACTIONS OF ALDEHYDES AND KETONES**

1. Oxidation.



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2. Reduction

(a) Reduction to alcohols.



Cyclopentanone Cyclopentane

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(c) Reductive amination.



#### 3. addition of derivatives of ammonia



Examples:



Benzaldehyde

Phenylhydrazine Benzaldehyde phenylhydrazone

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4. Addition of alcohols. Acetal formation.



Example:



5. Cannizzaro reaction.



Examples:



6. Halogenation of ketones.

