

Aldehydes, Ketones and Carboxylic Acids

Nomenclature of aldehydes and ketones -

Aldehydes:

Often called by their common names instead of IUPAC names.

Ketones:

Derived by naming two alkyl or aryl groups bonded to the carbonyl group

Alkyl phenyl ketones are usually named by adding the acyl group as prefix to phenone.

$$CH_3 - C - CH_3$$

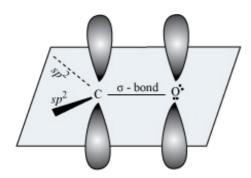
Acetone Acetophenone

IUPAC Nomenclature

- (i) For open-chain aliphatic aldehydes and ketones, IUPAC names are derived from the names of the corresponding alkanes by replacing the ending '-e' with '-al' and '-one' respectively.
- (ii) In the case of aldehydes, the longest chain is numbered starting from the carbon of the aldehydic group.
- (iii) In the case of ketones, the numbering begins from the end nearer to the carbonyl group.
- (iv) Substituents are prefixed in the alphabetical order along with the numerals indicating their positions in the carbon chain.
- (v) Same rule is applicable to cyclic ketones.
- (vi) If the aldehydic group is attached to a ring, then the suffix carbaldehyde is added to the full name of cyclohexane.

Example:

Structure of the carbonyl group –The carbonyl carbon atom is sp^2 hybridised and forms three bonds and one π bond.



C=O double bond is polarised due to higher electronegativity of oxygen relative to carbon.

Carbonyl carbon – an electrophile (Lewis acid)

Carbonyl oxygen – a nucleophile (Lewis base)

$$\begin{array}{c}
O \\
C \\
A
\end{array}$$

$$A \qquad B$$

Preparation of aldehydes and ketones:

(I) By oxidation of alcohols -

(i) Primary alcohols — □ → Aldehydes

(ii) Secondary alcohols _____ Ketones

(II) By dehydrogenation of alcohols

(i) Primary alcohols $Ag \text{ or } Cu \rightarrow Aldehydes$

(ii) Secondary alcohols AgarCu Ketones

Preparation of aldehydes:

(I) From acyl chloride –(Rosenmund reduction)

$$\begin{array}{c} O \\ \parallel \\ R-C-Cl \end{array} \xrightarrow{\begin{array}{c} H_2 \\ Pd-BaSO_4 \end{array}} \blacktriangleright RCHO \\ \end{array}$$

Acyl chloride

Aldehyde

(II) From nitriles – (Stephen reaction)

$$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3O^+} RCHO$$

(III) From esters -

Esters
$$\xrightarrow{1. DIBAL-H}$$
 Aldehydes

(IV) From hydrocarbons -

By oxidation of methylbenzene (toluene) (Etard reaction)

By side-chain chlorination, followed by hydrolysis

$$CH_3$$
 CH_2
 CHO
 CH_2
 CHO
 C

Gatterman-Koch reaction

Preparation of ketones:

(I) From acyl chlorides –

(II) From nitriles -

$$CH_{3}-CH_{2}-C\equiv N+C_{6}H_{5}MgBr\xrightarrow{ether}CH_{3}CH_{2}-C \nearrow NMgBr \xrightarrow{H_{3}O^{+}}C_{2}H_{5}-C \nearrow O$$

$$C_{6}H_{5}$$
Propiophenone (1-Phenylpropanone)

(III) From benzene or substituted benzene – (Friedel–Crafts acylation reaction)

$$+ Ar/R - C - Cl \xrightarrow{Anhyd. AlCl_3} Ar/R$$

Physical properties of aldehydes and ketones:

Boiling points:

- (i) Due to dipole—dipole interactions in aldehydes and ketones, they have higher boiling points than hydrocarbons and ethers of comparable molecular masses.
- (ii) Due to the presence of intermolecular H-bonding in alcohols, the boiling points of aldehydes and ketones are higher than those of alcohols of comparable molecular masses.

$$\overset{R}{\overset{\delta^{+}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}{\overset{\delta^{-}}}{\overset{\delta^{-}}{\overset{\delta^{-}}}{\overset{\delta^{-}}{\overset{\delta^{-}}}{\overset{\delta^{-}}{\overset{\delta^{-}}}{\overset{\delta^{-}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}}{\overset{\delta^{-}}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}}{\overset{\delta^{-}}}}{\overset{\delta^{-}}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}}{\overset{\delta^{-}}}}{\overset{\delta^{-}}}}{\overset{\delta^{-}}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}}{\overset{\delta^{-}}}}}}}}}}}}}}}}}}}}}}}}}}}}$$

Solubility: The solubility of aldehydes and ketones in water decreases with increase in the length of the alkyl chain.

Chemical reactions of aldehydes and ketones:

(A) Nucleophilic addition reactions -

Reactivity: Due to steric and electronic reasons, aldehydes are more reactive than ketones towards nucleophilic addition reactions.

(i) Addition of HCN

$$HCN + OH^{-} \longleftrightarrow : \overline{C}N + H_{2}O$$

(ii) Addition of Grignard reagents

$$\begin{bmatrix}
\delta^{+} & \delta^{-} & \delta^{-} & \delta^{+} \\
C & O & + & R - Mg - X
\end{bmatrix}$$

$$\begin{bmatrix}
C & O & Mg - X \\
R
\end{bmatrix}$$

$$\begin{bmatrix}
C & O & Mg - X \\
R
\end{bmatrix}$$

$$\begin{bmatrix}
C & O & Mg - X \\
R
\end{bmatrix}$$

$$\begin{bmatrix}
C & O & Mg - X \\
R
\end{bmatrix}$$

$$\begin{bmatrix}
C & O & Mg - X \\
R
\end{bmatrix}$$

(iii) Addition of alcohols

$$\begin{array}{c} R \\ R \\ \hline \\ C = O \end{array} + \begin{array}{c} CH_2OH \\ CH_2OH \end{array} \qquad \begin{array}{c} HCl \ gas \\ \hline dil. \ HCl \end{array} \qquad \begin{array}{c} R \\ R \\ \hline \\ C \\ O - CH_2 \end{array} + \begin{array}{c} H_2O \\ \hline \\ Ethylene \ glycol \ ketal \end{array}$$

(iv) Addition of ammonia and its derivatives

$$R$$
 $C = O + H_2N - Z$ R $C = N - Z + H_2O$

Z = alkyl, aryl, OH, NH₃, C₆H₅NH, NHCONH₂, etc

(B) Reduction -

(i) Reduction to alcohols

(a) Aldehydes
$$\xrightarrow{\text{NaBH}_4 \text{ or Li AlH}_4}$$
 Primary alcohols

(b) Ketones
$$\xrightarrow{\text{NaBH}_4 \text{ or Li AlH}_4}$$
 Secondary alcohols

(ii) Reduction to hydrocarbons

(a) Clemmenson reduction

$$c=0$$
 $\frac{Zn-Hg}{HCl}$ $CH_2 + H_2O$

(b) Wolf-Kishner reduction

$$C = O \xrightarrow{NH_2NH_2} C = NNH_2 \xrightarrow{KOH/ethylene glycol} CH_2 + N_2$$

- (C) Oxidation: Tests to distinguish between aldehydes and ketones –
- (i) **Tollen's test:** Tollen's reagent is Ammoniac silver nitrate solution. Ketones do not respond to this test.

$$R - CHO + 2 \left[Ag(NH_3)_2\right]^+ + 3OH^- \longrightarrow RCOO^- + 2Ag + 2H_2O + 4NH_3$$

(ii) Fehling's test: Ketones as well as aromatic aldehydes do not respond to this test.

$$R - CHO + 2Cu^{2+} + 5OH^{-} \longrightarrow RCOO^{-} + Cu_{2}O + 3H_{2}O$$

red-brown ppt

(iii) Oxidation by haloform reaction -

Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom undergo this reaction.

$$R = C - CH_3 \xrightarrow{NaOX} R - C - ONa + CHX_3 \quad (X = CI, Br, 1)$$

$$H = C - CH_3 \xrightarrow{NaOCI} R - C - ONa + CHX_3 \quad (X = CI, Br, 1)$$

$$H = C - CH_3 \xrightarrow{NaOCI} R - CHX_3 \quad (X = CI, Br, 1)$$

Reactions due to α-hydrogen -

Aldol condensation (aldol reaction): Aldehydes and ketones having at least one -hydrogen undergo this reaction.

$$\begin{array}{c} \text{CH}_3 \longrightarrow \text{CHO} & \stackrel{\text{dil. NaOH}}{\longleftarrow} \text{CH}_3 \longrightarrow \text{CH} \longrightarrow \text{CH}_2 \longrightarrow \text{CHO} \\ & \downarrow & \downarrow & \downarrow \\ & \text{OH} & & -\text{H}_2\text{O} \\ & 3 - \text{Hydroxybutanal} \\ & \text{(Aldol)} & \text{CH}_3 \longrightarrow \text{CH} \longrightarrow \text{CH} \longrightarrow \text{CHO} \\ & \text{But} - 2 - \text{enal} \\ & \text{(Aldol condensation product)} \end{array}$$

Cross aldol condensation: Aldol condensation between two different aldehydes and/or ketones

If both of them contain -hydrogen, then they give a mixture of four products.

Other reactions -

Cannizzaro reaction: Aldehydes that do not have an -hydrogen atom undergo this reaction.

Electrophilic substitution reaction:

$$\begin{array}{c|c} & & & \\ \hline & CHO & \hline & HNO_3/H_2SO_4 \\ \hline & 273-283 \text{ K} \\ \hline & O_2N \\ \end{array}$$
 CHO

m - Nitrobenzaldehyde

Uses of Aldehydes and Ketones

- (i) As solvents.
- (ii) As starting materials and reagents for the synthesis of other products.
- (iii) Acetaldehyde In the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs.
- (iv) Benzaldehyde In perfumery and in dye industries.
- (v) Butyraldehyde, vanillin, camphor, etc., are well known for their odours and flavours.
- (vi) Acetone and ethyl methyl ketone Common industrial solvents.

Nomenclature

In the IUPAC system, aliphatic carboxylic acids are named as follows:

- (i) By replacing the ending '- e' in the name of the corresponding alkane with '- oic acid'
- (ii) Carboxylic carbon is numbered one.
- (iii) If more than one carboxyl groups are present, then the ending '-e' of the alkane is retained.
- (iv) The number of carboxyl groups is indicated by adding prefix, *d*, tri, etc. to the term 'oic'.

For example:

(a) CH₃COOH:

Common name: Acetic acid

IUPAC name: Ethanoic acid

(b) HOOC -(CH₂)₄-COOH:

Common name: Adipic acid

IUPAC name: Hexanedioic acid

Methods of Preparation of Carboxylic Acid

(i) From primary alcohols

$$\begin{split} & \text{RCH}_2\text{OH} \xrightarrow{\text{1.Alkaline KMnO}_4} \text{RCOOH} \\ & \text{RCH}_2\text{OH} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+} \text{RCOOH} \\ & \text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{OH} \xrightarrow{\text{CrO}_3-\text{H}_2\text{SO}_4} \text{CH}_3(\text{CH}_2)_8\text{COOH} \\ & \text{1-Decanol} \end{split}$$

(ii) From primary aldehydes

$$RCHO \xrightarrow{[0]} R - COOH$$

Oxidising agents – HNO₃, KMnO₄, K₂Cr₂O₇

Mild oxidising agents - Tollen's reagent and Fehling's reagent

(iii) From alkyl benzenes

(iv) From nitriles and amides

$$R - CN \xrightarrow{H^+ \text{ or } OH^-} R - C - NH_2 \xrightarrow{H^+ \text{ or } OH^-} RCOOH$$
Nitrile RCOOH
Carboxylic acid

(v) From Grignard reagents

$$R - MgX + O = C = O \xrightarrow{Dry \text{ ether}} R - C \xrightarrow{\bar{O} \text{ MgX}} - \frac{H_3O^+}{C} + RCOOH$$
Grignard reagent Carboxylic acid

(vi) From acyl halides

RCOCI
Acyl halide
$$OH^{-}/H_{2}O$$

$$RCOOH + Cl^{-}$$

$$OH^{-}/H_{2}O$$

$$RCOO^{-} + Cl^{-}$$

$$RCOOH$$

(vii) From acyl anhydrides

(viii) From esters:

Acidic hydrolysis:

Basic hydrolysis:

$$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{COOC}_2\text{H}_5 & & \\ \hline \text{Ethyl butanoate} & & \text{CH}_3\text{CH}_2\text{CH}_2\text{COONa} + \text{C}_2\text{H}_5\text{OH} \\ & & \text{H}_3\text{O}^+ \\ \hline & \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \\ \hline & \text{Butanoic acid} \end{array}$$

Chemical reactions:

(I) Reactions that involve cleavage of O-H bond: Acidity

(a) Reactions with metals and alkalies

$$2R - COOH + 2Na \longrightarrow 2RCOONa + H_2$$
Sodium carboxylate
$$R - COOH + NaOH \longrightarrow R - COONa + H_2O$$

$$R - COOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2$$

- (b) Carboxylic acids are more acidic than phenols because the carboxylate ion is more stable than phenoxide ion.
- (c) Electron-withdrawing groups increase the acidity of carboxylic acid while electron-donating groups decrease the acidity.
- (II) Reactions that involve cleavage of C-OH bond
- (a) Formation of anhydride

Ethanoic acid

Ethanoic anhydride

(b) Esterification: Catalyst Conc. H₂SO₄ or HCl gas

$$RCOOH + R'OH \stackrel{H^+}{\longleftrightarrow} RCOOR' + H_2O$$

Acid Alcohol Ester Water

(c) Reactions with PCI₅, PCI₃, and SOCI₂

$$RCOOH + PCl_5 \longrightarrow RCOCl + PCl_3 + HCl$$

 $3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$
 $RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$

(d) Reaction with ammonia

$$\begin{array}{c} \text{CH}_3\text{COOH} + \text{NH}_3 & \longleftarrow \text{CH}_3\text{COO} \overset{-}{\text{N}} \text{H}_4 & \xrightarrow{\Delta} \text{CH}_3\text{CONH}_2 \\ \text{Ammonium acetate} & \text{Acetamide} \end{array}$$

COOH
$$COONH_4$$
 $CONH_2$
 $+ NH_3 \longrightarrow \Delta$

Ammonium Benzamide benzoate

(iii) Reactions that involve -COOH group

(a) Reduction

$$R - COOH \xrightarrow{(i)LiAlH_4/Ether \text{ or } B_2H_6} R - CH_2 - OH$$
(Alcohol)

(b) De-carboxylation

$$R - COONa \xrightarrow{NaOH-CaO} R - H + Na_2CO_3$$
(Alkane)

(c) Substitution reactions in the hydrocarbon part

(d) Halogenations

(i) Hell-Volhard-Zelinsky reaction

$$R-CH_2-COOH \xrightarrow{\text{(i) } X_2/Phosphorus} R-CH-COOH \\ | X \\ X = Cl, Br$$

α-Halocarboxylic acid

Carboxylic acids having an -hydrogen undergo this reaction.

(ii) Ring substitution

m-Nitrobenzoic acid

m-Bromobenzoic acid

Uses of Carboxylic Acids

- (i) Methanoic acid In rubber, textile, dyeing, leather and electroplating industries
- (ii) Ethanolic acid As a solvent and as a vinegar in food industry
- (iii) Hexanoic acid In the manufacture of nylon-6, 6
- (iv) Higher fatty acids For the manufacture of soaps and detergents
- (v) Esters of benzoic acid In perfumery
- (vi) Sodium benzoate As a food preservative