AND CARROYYLIC ACID **AND CARBOXYLIC ACIDS**

Being important constituents of fabrics, flavourings, plastics and drugs, carbonyl compounds are of utmost importance to organic chemistry while carboxylic acids are amongst the earliest organic compounds to be isolated from nature and are still known by their common names.

Structure and Nomenclature

Aldehvdes

- $R \overset{\square}{C} H$ where, R = H, alkyl or anyl group.
- In IUPAC system, aldehydes are named as alkanals.

- $R \ddot{C} R'$ where R and R' both can be same or different groups.
- In IUPAC system, they are named as alkanones.



Physical Properties

- Solubility in water ∞ 1/Molecular mass
- Compounds having upto four carbon atoms are soluble in water due to hydrogen bonding
- Due to dipole-dipole interactions their b.pts. are higher than the corresponding hydrocarbons or ethers but lesser than alcohols or carboxylic acids which have intermolecular H-bonding.
- Due to two electron donating alkyl groups, ketones have higher b.pts. than the corresponding aldehydes.

Distinction Tests				
Test	Aldehydes	Ketones		
Schiff's reagent	Pink colour	No colour		
Fehling's solution	Red ppt.	No ppt.		
Tollens' reagent	Silver mirror	No ppt.		
Sodium hydroxide	Brown resinous mass (except HCHO)	No reaction		
Alkaline sodium nitroprusside	A deep red colour (except HCHO)	Red colour which changes to orange		

Structure and Nomenclature

Carboxylic acids

- $R \stackrel{\text{ii}}{\text{C}}$ OH where, R = H, alkyl or aryl group.
- In IUPAC system, they are named as alkanoic acids.

Physical Properties

- Solubility in water $\propto \frac{1}{\text{Molecular mass}}$
- High b.pt. due to intermolecular hydrogen bonding.
- M.pts. and b.pts of aromatic acids are usually higher than those of aliphatic acids



Chemical Properties

- Acidity order: Carboxylic acids>Phenols>Alcohols
- EDG decreases the acidity and EWG increases the acidity.
- · More the electronegativity of the atom attached to the carboxyl group, more will be the acidity

Distinction Tests				
Test	Carboxylic acids	Phenols	Alcohols	
NaHCO ₃	Brisk effervescence of CO_2 gas	No reaction	No reaction	
FeCl ₃	Buff coloured ppt.	Violet , blue or red colour	No reaction	

Preparation

Oxidation of alcohols:

$$RCH_2OH + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4(dil.)} RCHO + H_2O$$

$$\stackrel{\text{(1° alcohol)}}{RCH(OH)R'} + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4(dil.)} RCOR' + H_2O$$

• Catalytic decomposition of carboxylic acids:

RCOOH + HOOCH
$$\xrightarrow{\text{MnO, 573 K}}$$
 RCHO + CO₂+ H₂O

RCOOH + HOOCR' $\xrightarrow{\text{MnO, 573 K}}$ RCOR' + CO₂+ H₂O

Hydroboration-oxidation of alkynes:

• Hydroboration-oxidation of alkynes:
$$R - C \equiv C - H \xrightarrow{B_2H_6} \begin{bmatrix} R - C = C - H \\ \parallel & \parallel H_2 \end{bmatrix} \xrightarrow{H_2O_2} \xrightarrow{OH^-}$$

$$R - C = C - H \Longrightarrow RCH_2C - H$$

$$H \longrightarrow OH \longrightarrow O$$

R-C=C-R'
$$\xrightarrow{B_2H_6}$$
 $R-C=C-R'$ $\xrightarrow{H_2O_2}$ $\xrightarrow{H_2O_2$

• Ozonolysis of alkenes:

$$RCH = C - R'' \xrightarrow{O_3} RCHO + R'' C = O$$

$$R'$$

$$R = \begin{pmatrix} R' \\ R - C - Cl & \frac{aq. \text{ KOH}}{\text{or Ba(OH)}_2} \end{pmatrix} R - C = O$$

$$Cl \qquad \qquad \left(\begin{cases} \text{Aldehyde when } R' = H \\ \text{Ketone when } R' = \text{alkyl group} \end{cases} \right)$$

Chemical Properties

Nucleophilic addition reactions:

Aldehydes > Ketones (steric and electronic reasons) HCHO > RCHO > PhCHO > RCOR > RCOPh > PhCOPh

Nucleophilic addition-elimination reactions:

$$(i) NH_3 \rightarrow C = NH + H_2O$$

$$(ii) \Delta \rightarrow C = N - Z + H_2O$$

$$(ii) \Delta \rightarrow C = N - Z + H_2O$$

$$(Z = \text{alkyl, aryl,} -OH, -NH_2, -NHC_6H_5,$$

$$(D = NO_2, -NH - C - NH -$$

$$\begin{array}{c} RCHO \xrightarrow{\text{Reduction}} \Rightarrow RCH_2OH \\ RCOR' \xrightarrow{\text{Reduction}} \Rightarrow RCH(OH)R' \end{array} |_{\text{LiAlH}_4 \text{ or NaBH}_4)}$$

 $\begin{array}{c} RCHO \xrightarrow{Reduction} > RCH_3 \\ RCOR' \xrightarrow{Reduction} > RCH_2R' \end{array} \bigg|_{HI/Red P)} (Zn \cdot Hg/HCl, NH_2NH_2/KOH, HI/Red P)$ $\begin{array}{c}
\text{Oxidation} & \xrightarrow{\text{O}} & \text{RCOOH} \text{ (Even with mild oxidising agents)} \\
\text{(same no. of C atoms)}
\end{array}$

 $RCOR' \xrightarrow{Oxidation} RCOOH$ (With strong oxidising agents) (lesser no. of C atoms)

Haloform reaction:

Given by compounds having CH3CO-group or CH₃CH(OH)-group

$$RCOCH_3 \xrightarrow{NaOX} RCOONa + CHX_3$$
Haloform

• Cannizzaro reaction:

Preparation

• Oxidation of 1° alcohols:
$$RCH_2OH \xrightarrow{alk. KMnO_4} RCHO \xrightarrow{[O]} RCOOH$$

• Hydrolysis of nitriles and amides :

RCN + 2H₂O
$$\frac{\text{H}^{+}\text{or}}{\text{OH}^{-}}$$
 RCOOH + NH₃
RCONH₂ $\frac{\text{H}_{2}\text{O}}{\text{heat}}$ RCOOH + NH₃

• From Grignard reagents :

$$CO_2 + CH_3MgBr \xrightarrow{Dry ether} CH_3COOH + Mg(OH)Br$$

• Hydrolysis of esters :

$$RCOOR' + H_2O \xrightarrow{H^+ \text{ or OH}^-} RCOOH + R'OH$$

• Carbonylation (Koch reaction) of alkenes :

• Carbonylation (Koch reaction) of alkenes:

$$CH_2 = CH_2 + CO + H_2O \xrightarrow{\text{H}_3\text{PO}_4, 573-673 \text{ K}} CH_3\text{CH}_2\text{COOH}$$

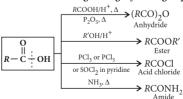
• From methyl ketones:

O

$$CH_3CH_2 - C - CH_3 + 3NaOI \xrightarrow{HCl} CH_3CH_2COOH + CHI_3 + 2NaOI$$

Chemical Reactions

Reactions involving cleavage of —OH group :



Reactions involving proton of —OH group:

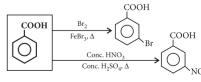
$$\begin{array}{c|c}
Na & \rightarrow 2RCOONa + H_2 \\
NaOH & \rightarrow RCOONa + H_2O \\
R - C - OH & \rightarrow RCOONa + CO_2 + H_2O \\
NaHCO_3 & \rightarrow RCOONa + CO_2 + H_2O
\end{array}$$

• Reactions involving>C=O group:

$ \begin{array}{ c c c c }\hline \hline O \\ \hline R & \hline C & OH \\\hline \hline & (i) \operatorname{LiAlH}_4/\text{ether or } \operatorname{B}_2\operatorname{H}_6/\text{ether} \\ \hline & (ii) \operatorname{H}_3\operatorname{O}^+ \ (\text{Reduction}) \\ \hline \end{array} $	\rightarrow RCH ₂ OH
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• Ring substitution in aromatic acids:

—COOH group is deactivating and *meta* directing.



Reactions involving —COOH group:



 $Reactions\ involving\ -R\ group:$

$$R \xrightarrow{\text{O}} \text{II} \xrightarrow{\text{(i) } X_2/\text{Red P}} R - \text{CH} - \text{COOH}$$

$$\xrightarrow{\text{(ii) } H_2\text{O}} R \xrightarrow{\text{CH} \text{-locarboxylic acid}} R \xrightarrow{\text{-locarboxylic acid}} R \xrightarrow{\text{CH} \text{-locarboxylic acid}} R \xrightarrow{\text{CH} \text{-locarboxylic acid}} R \xrightarrow{\text{-locarboxylic acid}} R \xrightarrow{\text{$$