CONCEPT MAP

ALDEHYDES, KETONES 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.

ALDEHYDES AND KETONES

Structure and Nomenclature

Aldehydes

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

Ketones

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

Preparation

- ***Oxidation of alcohols:***

$$\underset{(1^\circ\text{ alcohol})}{RCH_2OH} + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4(\text{dil.})} RCHO + H_2O$$

$$\underset{(2^\circ\text{ alcohol})}{RCH(OH)R'} + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4(\text{dil.})} RCOR' + H_2O$$

- ***Catalytic decomposition of carboxylic acids:***

$$RCOOH + HOOCH \xrightarrow{MnO,\ 573\ K} RCHO + CO_2 + H_2O$$

$$RCOOH + HOOCR' \xrightarrow{MnO,\ 573\ K} RCOR' + CO_2 + H_2O$$

- ***Hydroboration-oxidation of alkynes:***

$$\underset{\text{Terminal alkyne}}{R-C\equiv C-H} \xrightarrow[THF]{B_2H_6} \left[\begin{matrix} R-C=C-H \\ \quad\ \ H \quad BH_2 \end{matrix}\right] \xrightarrow[OH^-]{H_2O_2} R-\underset{H}{C}=\underset{OH}{C}-H \rightleftharpoons RCH_2\underset{O}{\underset{\|}{C}}-H$$

$$R-C\equiv C-R' \xrightarrow[THF]{B_2H_6} \left[\begin{matrix} R-C=C-R' \\ \quad\ \ H \quad BH_2 \end{matrix}\right] \xrightarrow[OH^-]{H_2O_2} R-\underset{H}{C}=\underset{OH}{C}-R' \rightleftharpoons RCH_2\underset{O}{\underset{\|}{C}}-R'$$

- ***Ozonolysis of alkenes:***

$$RCH=\underset{R'}{C}-R'' \xrightarrow[H_2O,\ Zn]{O_3} RCHO + \begin{matrix}R'\\R''\end{matrix}\!\!>C=O$$

- ***From gem-dihalides:***

$$R-\overset{R'}{\underset{Cl}{C}}-Cl \xrightarrow[\text{or } Ba(OH)_2]{aq.\ KOH} R-\overset{R'}{C}=O$$

(Aldehyde when R' = H
Ketone when R' = alkyl group)

Physical Properties

- Solubility in water $\propto \dfrac{1}{\text{Molecular mass}}$
- 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.

Chemical Properties

- ***Nucleophilic addition reactions:***

$$>C=O + :Nu^- \underset{}{\overset{slow}{\rightleftharpoons}} >C\begin{matrix}O^-\\Nu\end{matrix} \underset{}{\overset{H^+,\ fast}{\rightleftharpoons}} >C\begin{matrix}OH\\Nu\end{matrix}$$

- ***Reactivity order:***
  Aldehydes > Ketones (steric and electronic reasons)
  HCHO > RCHO > PhCHO > RCOR > RCOPh > PhCOPh
- ***Nucleophilic addition-elimination reactions:***

$$\boxed{>C=O} \xrightarrow[(ii)\ \Delta]{(i)\ NH_3} \underset{\text{Imine}}{>C=NH} + H_2O$$

$$\boxed{>C=O} \xrightarrow[(ii)\ \Delta]{(i)\ NH_2-Z} >C=N-Z + H_2O$$

(Z = alkyl, aryl, $-OH$, $-NH_2$, $-NHC_6H_5$, $-NH-C_6H_3(NO_2)_2$ (2,4-dinitrophenyl), $-NH-\overset{O}{\overset{\|}{C}}-NH_2$)

- ***Reduction and oxidation:***

$$RCHO \xrightarrow{\text{Reduction}} RCH_2OH$$

$$RCOR' \xrightarrow{\text{Reduction}} RCH(OH)R'$$

(H_2/Ni or Pt or Pd, $LiAlH_4$ or $NaBH_4$)

$$RCHO \xrightarrow{\text{Reduction}} RCH_3$$

$$RCOR' \xrightarrow{\text{Reduction}} RCH_2R'$$

(Zn-Hg/HCl, NH_2NH_2/KOH, HI/Red P)

$$RCHO \xrightarrow{\text{Oxidation}} RCOOH$$ (Even with mild oxidising agents) (same no. of C atoms)

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

- ***Haloform reaction:***
  Given by compounds having CH_3CO-group or $CH_3CH(OH)-$group

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

- ***Aldol condensation:***

$$\underset{\text{(Aldehyde or ketone having }\alpha\text{-hydrogen)}}{CH_3-\overset{O}{\overset{\|}{C}}-H + H-\overset{H}{\underset{H}{C}}-\overset{H}{C}=O} \xrightarrow{\text{dil. NaOH}} \underset{\text{Aldol}}{CH_3-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{C}=O}$$

- ***Cannizzaro reaction:***

$$\underset{\text{(Aldehyde or ketone having no }\alpha\text{-hydrogen)}}{HCHO + HCHO} \xrightarrow{\text{KOH (conc.)}} CH_3OH + HCOO^-K^+$$

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

CARBOXYLIC ACIDS

Structure and Nomenclature

Carboxylic acids

- $R-\overset{O}{\overset{\|}{C}}-OH$ where, R = H, alkyl or aryl group.
- In IUPAC system, they are named as *alkanoic acids*.

Preparation

- ***Oxidation of 1° alcohols:***

$$RCH_2OH \xrightarrow[{[O]}]{\text{alk. }KMnO_4} RCHO \xrightarrow[\text{acid}]{[O]} RCOOH$$

- ***Hydrolysis of nitriles and amides:***

$$RCN + 2H_2O \xrightarrow[OH^-]{H^+\text{ or}} RCOOH + NH_3$$

$$RCONH_2 \xrightarrow[\text{heat}]{H_2O} RCOOH + NH_3$$

- ***From Grignard reagents:***

$$CO_2 + CH_3MgBr \xrightarrow[H^+,\ H_2O]{\text{Dry ether}} CH_3COOH + Mg(OH)Br$$

- ***Hydrolysis of esters:***

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

- ***Carbonylation (Koch reaction) of alkenes:***

$$CH_2=CH_2 + CO + \underset{\text{(steam)}}{H_2O} \xrightarrow[\text{Under pressure}]{H_3PO_4,\ 573-673\ K} CH_3CH_2COOH$$

- ***From methyl ketones:***

$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + 3NaOI \xrightarrow[-NaCl]{HCl} CH_3CH_2COOH + CHI_3 + 2NaOH$$

Physical Properties

- Solubility in water $\propto \dfrac{1}{\text{Molecular mass}}$
- 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.

Chemical Reactions

- ***Reactions involving cleavage of $-OH$ group:***

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[P_2O_5,\ \Delta]{RCOOH/H^+,\ \Delta} \underset{\text{Anhydride}}{(RCO)_2O}$$

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{R'OH/H^+} \underset{\text{Ester}}{RCOOR'}$$

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{or }SOCl_2\text{ in pyridine}]{PCl_3\text{ or }PCl_5} \underset{\text{Acid chloride}}{RCOCl}$$

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NH_3,\ \Delta} \underset{\text{Amide}}{RCONH_2}$$

- ***Reactions involving proton of $-OH$ group:***

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{Na} 2RCOONa + H_2$$

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NaOH} RCOONa + H_2O$$

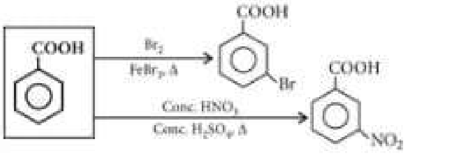
$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{Na_2CO_3} 2RCOONa + CO_2 + H_2O$$

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NaHCO_3} RCOONa + CO_2 + H_2O$$

- ***Reactions involving $>C=O$ group:***

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[(ii)\ H_3O^+\ \text{(Reduction)}]{(i)\ LiAlH_4/\text{ether or }B_2H_6/\text{ether}} RCH_2OH$$

- ***Ring substitution in aromatic acids:***
  $-COOH$ group is deactivating and *meta* directing.



- ***Reactions involving $-COOH$ group:***

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\Delta\ \text{(Decarboxylation)}]{\text{NaOH and CaO}} RH + Na_2CO_3$$

- ***Reactions involving $-R$ group:***

$$RCH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[(ii)\ H_2O]{(i)\ X_2/\text{Red P}} \underset{\alpha\text{-Halocarboxylic acid (Hell-Volhard Zelinsky reaction)}}{R-\underset{X}{CH}-COOH}$$

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