

ORGANIC CHEMISTRY

ENTHUSIAST | LEADER | ACHIEVER



STUDY MATERIAL

Oxygen Containing Compounds

ENGLISH MEDIUM





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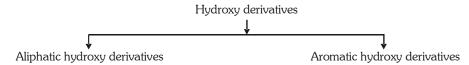
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OXYGEN CONTAINING COMPOUND

1.0 HYDROXY DERIVATIVES



1.1 Aliphatic Hydroxy Derivatives

Hydroxy derivatives in which —OH is directly attached to sp³ 'C' (Alcoholic compounds).

1.2 Aromatic Hydroxy Derivatives

Hydroxy derivatives in which —OH is directly attached to sp² 'C' or benzene ring (Phenolic compounds).

Aliphatic hydroxy derivatives :

(a) Classification according to number of -OH groups:

- (i) Monohydric [one -OH] \longrightarrow CH₃CH₂—OH (ii) Dihydric [two -OH] \longrightarrow CH₂ - CH₂ OH OH (iii) Trihydric [three -OH] \longrightarrow CH₂ - CH - CH₂ OH OH OH

(b) Classification according to nature of carbon:

(i) p or
$$1^{\circ}$$
 – alcohol — CH₃CH₂ – OH

(ii) s or
$$2^{\circ}$$
 – alcohol — (CH₃)₂CH – OH

(iii) t or
$$3^{\circ}$$
 – alcohol — (CH₃)₃C – OH

2.0 MONOHYDRIC ALCOHOL

2.1 General Methods of Preparation

(i) From alkanes (By oxidation):

$$(CH_3)_3$$
 C — H $\xrightarrow{H^{\oplus}/KMnO_4}$ $(CH_3)_3$ C — OH

(ii) From alkenes:

(a) By hydration:

$$CH_3$$
— CH = CH_2 $\xrightarrow{H^{\oplus}}$ CH_3 CH CH_3 OH

(b) By hydroboration oxidation:

$$CH_{3} - CH = CH_{2} \xrightarrow{(1)BH_{3}, THF} CH_{3} - CH_{2} - CH_{2} - CH_{2}$$
 (1° alcohol)

(c) By oxymercuration demercuration:

$$CH_3$$
— $CH=CH_2$ $\xrightarrow{\text{(i)} Hg(OAc)_2, H_2O}$ $CH_3 - CH - CH_3$ OH



(iii) From alkyl halides (By hydrolysis):

$$CH_3$$
— CH_2 — Cl $\xrightarrow{Aq. KOH}$ CH_3CH_2 — OH

(iv) From carbonyl compounds (By reduction):

$$>C = O$$
 Reducing agent $>CH$ — OH

GOLDEN KEY POINTS

Reducing agents may be,

LiAlH₄/H[⊕]

NaBH₄/H[⊕]

Na + EtOH

Ni/H₂

$$\text{CH}_{3}\text{--CH=CH---CHO} \xrightarrow{\quad \text{LiAlH}_{4} \quad } \text{CH}_{3}\text{--CH=CH---CH}_{2}\text{--OH}$$

Crotonaldehyde

(v) From ethers:

(vi) From acid and derivatives (By reduction):

Note: Amide on reduction gives amine not alcohol.



(vii) From esters (By hydrolysis):

(a) By alkaline hydrolysis:

$$\begin{array}{ccc} \text{R-C-OR} & \xrightarrow{\quad NaOH \quad} & \text{R-C-ONa} + \text{R-OH} \\ \parallel & \parallel & \parallel \\ \text{O} & & \text{O} \end{array}$$

Mechanism:

$$R-C-OR \xrightarrow{HO^{\ominus}} R-C \xrightarrow{(NaOH)} R-C \xrightarrow{(OR)} R-C \xrightarrow{R-C} R-C + RO \xrightarrow{(SA)} R-C \xrightarrow{(SA)} R-C \xrightarrow{(SA)} R-C \xrightarrow{(SA)} R-C-O+ROH$$

$$R-C-ONa+ROH \xrightarrow{Na} R-C-O+ROH \xrightarrow{Na} R-C-O+ROH$$

$$CH_3-C-OC_2H_5 \xrightarrow{(NaOH)} CH_3-C-ONa+C_2H_5OH$$

Hydrolysis is Nucleophilic substitution reaction (NSR) and Order of reaction is 2. Alkaline hydrolysis is also called as saponification

$$Ph$$
— $COOC_2H_5$ $\xrightarrow{HO^{\odot}}$ Ph — $COO^{\circ}_2+C_2H_5OH$

(b) By acidic hydrolysis:

(viii) From p-amines:

$$\begin{array}{ccc} R - NH_2 & \xrightarrow{NaNO_2 + HCl(aq.)} & R - OH + N_2 \\ \\ CH_3CH_2 - NH_2 & \xrightarrow{HNO_2} & CH_3CH_2 - OH + N_2 \end{array}$$

Mechanism:

$$CH_{3}CH_{2} - NH_{2} \xrightarrow{NaNO_{2} + HCl} CH_{3}CH_{2} - \stackrel{\oplus}{N_{2}}\stackrel{O}{Cl} \longrightarrow CH_{3}\stackrel{\oplus}{CH_{2}} + N_{2} + \stackrel{\ominus}{Cl}$$
(Unstable)

$$\begin{array}{c} & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ &$$

Intermediate is carbocation so rearrangement may be possible.



- Illustrations

NaNO₂+HCl 2 Illustration 1. CH₃CH₂CH₂—NH₂ -

Solution. Mechanism:

Exception :
$$CH_3-NH_2 \xrightarrow{HNO_2} CH_3-O-CH_3$$

(ix) From Grignard reagent:

(a) p-alcohol:

$$R-MgX + [O] \longrightarrow R-O-MgX \xrightarrow{H_2O} R-OH$$

$$[Same C-p-alcohol]$$

$$R-MgX + H-C-H \longrightarrow H-C-H$$

$$OMgX \longrightarrow OH [one C more p-alcohol]$$

$$R-MgX + CH_2-CH_2 \longrightarrow CH_2-CH_2$$

$$OMgX \longrightarrow OH$$

$$[two C more p-alcohol]$$

(b) s-alcohol:

(c) t-alcohol:

$$R - MgX + R - C - R \longrightarrow R - C - R \xrightarrow{H_2O} R - C - R$$

$$R - MgX + R - C - OR \longrightarrow R - C - R \xrightarrow{R - MgX} R - C - R$$

$$R - MgX + R - C - OR \longrightarrow R - C - R \xrightarrow{R - MgX} R - C - R$$

$$O \longrightarrow O \longrightarrow O \longrightarrow O$$

Physical properties:

- (i) C_1 to C_{11} are colourless liquids and higher alcohols are solids.
- (ii) Density of monohydric alcohol is less than H₂O.
- (iii) Density ∝ mol. wt. (for monohydric alcohol).



(iv) **Solubility**: C_1 to C_3 and t-butyl alcohol is completely soluble in H_2O due to H-bonding.

solubility
$$\propto \frac{\text{No. of side chains}}{\text{molecular weight}}$$

Order of solubility:

$$C_4H_9OH$$
 > $C_5H_{11}OH$ > $C_6H_{13}OH$

[Number of OH increases, H-bonding increases]

(v) **Boiling points :** BP
$$\propto \frac{\text{molecular weight}}{\text{No.of side chains}}$$

Orber of BP :
$$C_4H_9OH$$
 < $C_5H_{11}OH$ < $C_6H_{13}OH$

[Number of OH increases, H-bonding increases]

- Illustrations

Illustration 2. Boiling point of alcohol is more than corresponding ether. Why?

Solution. H-bonding in alcohol.

Illustration 3. Boiling point of alcohol is less than corresponding carboxylic acid. Why?

Solution. Dimer formation in carboxylic acid.

2.3 **Chemical Properties**

Monohydric alcohol shows following reactions

- (A) Reaction involving cleavage of $O \neq H$
- (B) Reaction involving cleavage of $C \neq OH$
- (C) Reaction involving complete molecule of alcohol



(A) Reaction involving cleavage of $O \dotplus H$: Reactivity order (Acidic nature) is

 CH_3 —OH > CH_3CH_2 —OH > $(CH_3)_2CH$ —OH > $(CH_3)_3C$ —OH

(i) Acidic nature:

 $H_2O > R - OH > CH = CH > NH_3$ (Acidic strength)

Alcohols are less acidic than H₂O and neutral for litmus paper and give H₂ with active metals (Na, K)

$$R$$
—OH + Na \longrightarrow R —ONa + $\frac{1}{2}H_2$

(ii) Alkylation:

$$R \text{--OH} \xrightarrow{\text{Na}} \qquad \qquad R \text{--ONa} \qquad \xrightarrow{\text{R--X}} \qquad R \text{--O--R}$$

(Williamson synthesis)

(iii) Acylation:

(Acylation)

$$R - OH + Cl - C - CH_3 \longrightarrow R - O - C - CH_3$$

(Acetylation)

$$\begin{array}{ccc}
OH & & & & O-C-CH_3 \\
\hline
O & & & & & & & & & & & & \\
\hline
O & & & & & & & & & & \\
\hline
O & & & & & & & & & \\
\hline
O & & & & & & & & \\
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O & & & & & & & \\
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O & & & & & & \\
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O & & & & & & \\
\hline
O & & & \\
\hline
O & & &$$

Salicylic acid

Acetoxy benzoic acid

Acetyl salicylic acid

Aspirin [Used as analgesic and antipyretic]

(iv) Benzoylation: (Schotten Baumann's Reaction):

(Benzoylation)

(v) Esterification:

Conc. H₂SO₄ is used as catalyst and dehydrating agent.



Mechanism:

Ex.
$$CH_3$$
- C - $OH + H$ - OC_2H_5 $\xrightarrow{conc. H_2SO_4}$ CH_3 - C - OC_2H_5 + H_2O
 O

Ex. Ph-C+OH + H-OC₂H₅
$$\xrightarrow{\text{conc. H}_2SO_4}$$
 Ph - C - OC₂H₅ + H₂O

Dry HCl can also be used as dehydrating agent.

Ex.
$$CH_3$$
— C — $OH + H$ — OC_2H_5 $\xrightarrow{dry HCl}$ CH_3 — C — OC_2H_5 + H_2O

GOLDEN KEY POINTS

- Reactivity for esterification $\propto \frac{1}{\text{Steric hindrance}}$
- Reactivity of R OH [If acid is same]: $CH_3 OH > 1^\circ > 2^\circ > 3^\circ$ alcohol
- Reactivity of RCOOH [If alcohol is same]:

(vi) Reaction with CHCH:

Methylal

$$CH = CH + 2CH_{3}CH_{2} - OH \xrightarrow{BF_{3}/HgO} CH_{3}CH \xrightarrow{OC_{2}H_{5}}$$

$$CH_{3}CH \xrightarrow{OC_{2}H_{5}}$$

Ethylal



(vii) Reaction with carbonyl compounds:

$$R-CHO + 2R-OH \xrightarrow{H^{\oplus}} R-CH \xrightarrow{OR} OR$$

$$Acetal$$

$$R-C-R+2R-OH \xrightarrow{H^{\oplus}} R \xrightarrow{C} OR$$

$$O$$

$$CH_{3}CHO + 2CH_{3}-OH \xrightarrow{H^{\oplus}} CH_{3}CH \xrightarrow{OCH_{3}} OCH_{3}$$

(viii) Reaction with Grignard reagent:

$$R-MgX + H-OR \longrightarrow R-H + Mg < X OR$$

(B) Reaction involving cleavage of $C \stackrel{i}{\longrightarrow} OH$: Reactivity order or basic nature is

$$CH_3$$
—OH < CH_3CH_2 —OH < $(CH_3)_2CH$ —OH < $(CH_3)_3$ C—OH

(i) Reaction with halogen acid:

$$R-CH_2-OH + HCl \xrightarrow{ZnCl_2} R-CH_2-Cl + H_2O$$

Reactivity order of the acids is HI > HBr > HCl

(ii) Reaction with phosphorous halides:

$$3R$$
—OH + PCl₃ \longrightarrow $3RCl + H3PO3$
 R —OH + PCl₅ \longrightarrow R —Cl + POCl₂ + HCl

(iii) Reaction with thionyl chloride (SOCl₂):

$$R$$
—OH + $SOCl_2$ — $Pyridine$ — R —Cl + SO_2 ↑ + HCl (gas)

(iv) Reaction with NH₃: Alumina (Al₂O₃) is used as dehydrating agent.

$$R + OH + HNH_2$$
 $\xrightarrow{Al_2O_3}$ $R-NH_2 + H_2O$

- (C) Reaction involving complete molecule of alcohol:
- (i) Dehydration: Removal of H₂O
 - (a) Intermolecularly removal of H₂O [formation of ether]
 - (b) Intramolecularly removal of H₂O [formation of alkene]

$$C_{2}H_{5}-OH+H_{2}SO_{4} \xrightarrow{170^{\circ}C} C_{2}H_{5}-O-C_{2}H_{5} \text{ (Williamson's continuous etherification)}$$

$$C_{2}H_{5}-OH+H_{2}SO_{4} \xrightarrow{170^{\circ}C} CH_{2}=CH_{2} \text{ (Elimination)}$$

$$C_{2}H_{5}OH+Al_{2}O_{3} \xrightarrow{(Alumina)} 350^{\circ}C \xrightarrow{CH_{2}=CH_{2}} CH_{2}$$

Ease of dehydration follows the order : 3° ROH > 2° ROH > 1° ROH



(ii) Catalytic Dehydrogenation:

(iii) Oxidation:

Carbonyl group goes with smaller alkyl group [Popoff's rule suggested for oxidation of unsymmetrical ketones]

(iv) Distinction between 1° , 2° and 3° alcohols :

(a) Lucas test: A mixture of HCl(conc.) and anhydrous ZnCl₂ is called Lucas reagent.

p-alcohol
$$\xrightarrow{ZnCl_2+HCl}$$
 No turbidity at room temp. [On heating within 30 minutes.] s-alcohol $\xrightarrow{ZnCl_2+HCl}$ Turbidity appears within 5 minutes. t-alcohol $\xrightarrow{ZnCl_2+HCl}$ Turbidity appears within 2-3 sec.



(b) Victor - Meyer test:

Sodium nitrolate (Red)

No reaction (Remains blue)

(C) Dichromate test:

(v) Distinction between CH₃ - OH and C₂H₅OH

	CH ₃ OH	CH ₃ CH ₂ OH
B.P.	65℃	78℃
I ₂ + NaOH	No ppt	Yellow ppt of CHI ₃
Cu/300°C	Smell of formalin [HCHO]	No smell
Salicylic acid	Smell like oil of wintergreen	No smell



$$\begin{array}{c|cccc} OH & OH \\ \hline COOCH_3 & Methyl salicylate \\ (smell like oil of wintergreen) \\ \hline OH & OH \\ \hline O & COOH & COOPh \\ \hline COOPh & Phenyl salicylate \\ Salol (Antiseptic) \\ \hline O & COOH & COOPh \\ \hline COOH & COOPh \\ \hline COOH & COOPh \\ \hline COOPh & COOPH \\ C$$

BEGINNER'S BOX-1

- 1. Which of the following reactions of alkanols does not involve C-O bond breaking
 - (1) CH₂CH₂OH + SOCl₂

(2) CH₃CH(OH)CH₃ + PBr₃

(3) CH₃CH₂OH + CH₃COOH

- (4) ROH + HX
- 2. Which of the following alkanols is most soluble in water
 - (1) 1-Butanol
- (2) 2-Butanol
- (3) Isobutyl alcohol
- (4) t-Butyl alcohol

 $CH_{3}CH_{2}CH_{2}\text{-}OH \xrightarrow{PCl_{3}} A \xrightarrow{Alc.KOH} B \xrightarrow{H_{3}O^{\oplus}} C$ 3.

Find product 'C' is

(1) $CH_3CH=CH_2$

(2) CH₃-CH-CH₃ (3) CH₃-CH-CH₃ OH

(4) CH₃CH₂CH₂-Cl

Important facts about alcohols

- Toxicity [ethyl alcohol < Iso propyl alcohol < methyl alcohol]
- Absolute alcohol: Ethyl alcohol-99.5%-100%
- (iii) Power alcohol: Rectified spirit + C_6H_6 + Petrol for generation of power
- (iv) Methylated spirit: Methanol + Pyridine + mineral naptha + rectified spirit.
- (v) 70% CH₃OH is known as wood spirit.
- (vi) 90% C₂H₅OH is known as Raw spirit.
- (vii) C₂H₅OH is technically called WASH.
- (viii) Rectified spirit contains 95.5% alcohol and 4.5% H₂O.

GOLDEN KEY POINTS

Oxidation by HIO₄ [per iodic acid] or (CH₃COO)₄Pb [lead tetraacetate] :

$$\begin{array}{ccc} \mathrm{CH_2} \stackrel{+}{-} \mathrm{CH_2} & \xrightarrow{} & \mathrm{HCHO} + \mathrm{HCHO} \\ | & | & | & \\ \mathrm{OH} & \mathrm{OH} & \end{array}$$

(Ethylene glycol)

$$\begin{array}{c|cccc} CH_2 & CH & CH_2 & \xrightarrow{HIO_4} & HCHO+HCOOH+HCHO \\ | & | & | & | \\ OH & OH & OH \\ & & Glycerol \end{array}$$



Condition for oxidation by HIO₄ or (CH₃COO)₄Pb

- (i) At least 2 —OH or 2 >C=O or 1 —OH and 1 >C=O should be at vicinal carbons.
- (ii) One HIO_4 breaks one C-C bond and adds one -OH to each carbon .

Ex.
$$CH_3$$
— CH_3 — CH_3 — CH_3 — CH_3 — CH_3 — CH_3 — CH_4 — CH_5 — CH_5 — CH_5 — CH_5 — CH_5 — CH_6 — CH_7 — CH_7 — CH_8 — $CH_$

Ex.
$$O \\ CH_3-C-CH-CH_2-C-H \\ O \\ OH \\ O \\ CH_3-C-OH + HO-CHCH_2-C-H \\ O \\ OH \\ CH_3-C-OH + HO-CHCH_2-C-H \\ O \\ OH \\ CH_3COOH + CHO - CH_2-CHO \\ CH_3COOH + CHO - CHO$$

Ex.
$$CHO$$
 CHO CHO CHO CHO CHO CHO CHO CHO $COOH$ $COOH$ $COOH$ $COOH$ CH_2 CHO C

4.0 AROMATIC HYDROXY DERIVATIVES

Phenolic compounds : Compounds in which —OH group is directly attached to sp²c [Benzene ring]

All phenolic compounds give colour with neutral FeCl₃.

Ph—OH
$$\xrightarrow{\text{neutral FeCl}_3}$$
 Violet colour CH_3CH_2 —OH $\xrightarrow{\text{neutral FeCl}_3}$ No colour



PHENOL (C₆H₅OH)

Phenol is also known as carbolic acid. In phenol —OH group is attached with sp² hybridised carbon.

4.1 **General Methods of Preparation**

(1) From benzene sulphonic acid: When sodium salt of benzene sulphonic acid is fused with NaOH phenol is obtained.

$$C_6H_5SO_3Na \xrightarrow{(1)NaOH, \Delta\&Pr.} C_6H_5OH + Na_2SO_3$$

(2) From benzene diazonium chloride: When benzene diazonium chloride solution is warmed with water, phenol is obtained with evolution of nitrogen.

$$\begin{array}{c|c} N_2Cl & OH \\ \hline O & \underbrace{ \begin{array}{c} (Steam \ distilled) \\ \Delta \end{array} } \end{array} \begin{array}{c} OH \\ \hline \end{array} + N_2 + HCl$$

(3) By distilling a phenolic acid with sodalime (decarboxylation):

$$\begin{array}{c}
OH \\
COOH \\
\hline
\end{array}
\begin{array}{c}
OH \\
\hline
\end{array}$$
+ Na₂CO₃

Salicylic acid

(4) From Grignard reagent: The Grignard reagent on reaction with oxygen and subsequent hydrolysis yields phenol.

$$C_6H_5MgBr \xrightarrow{[O]} C_6H_5OMgBr \xrightarrow{H_2O} C_6H_5OH + Mg < OH$$

(5) From benzene:

R—Cl

$$\bigcirc + [O] \xrightarrow{V_2O_5} \bigcirc$$

Aq. NaOH

(6) From chloro benzene:

R—Cl
$$\xrightarrow{\text{Aq. NaOH}}$$
 R—OH [NSR]

Ph—Cl $\xrightarrow{\text{(1) Aq. NaOH, } \Delta \& Pr}$ Ph—OH [NSR at high temperature]

Order for NSR:

Cl
$$O_2$$
 O_2 O_3 O_4 O

2, 4, 6-Trinitrophenol (Picric acid)

- (7) Industrial preparation of phenol: Phenol can be prepared commercially by:
 - (a) Cumene
 - (b) Dow's process
- (a) From cumene (Isopropyl benzene): Cumene is oxidised with oxygen into cumene hydroperoxide in presence of a catalyst. This is decomposed by dil. H₂SO₄ into phenol and acetone.

(b) Dow process: This process involves alkaline hydrolysis of chloro benzene-(obtained by above process) followed by acidification.

$$C_6H_5Cl \xrightarrow{(1)\text{NaOH}, 623\text{K}, 300\text{atm}} + \text{NaCl}$$

BEGINNER'S BOX-2

- 1. Which of the following compounds does not show phenolic properties:-
 - (1) $\bigcirc \stackrel{CH-CH_3}{\bigcirc \stackrel{}{\mid}}$ OH

(2) OH OH

(3) OH OH

- (4) OH CH₂OH
- **2.** The number of dihydric phenols possible with the molecular formula $C_6H_6O_2$ is :-
 - (1) 2

(2) 3

(3) 4

(4)5

4.2 Physical Properties

- (i) Phenol is a colourless, crystalline solid.
- (ii) It attains pink colour on exposure to air and light. (slow oxidation)

$$C_6H_5OH-----O=\bigcirc O$$

Phenoquinone(pink colour)

- (iii) It is poisonous in nature but acts as antiseptic and disinfectant.
- (iv) Phenol is slightly soluble in water, readily soluble in organic solvents.
- (v) Solublity of phenol in water is much lower than alcohols because of larger hydrocarbon part in the molecule.
- (vi) Due to intermolecular H-Bonding, phenol has relatively high boiling point than the corresponding hydrocarbons, anyl halides.

4.3 Chemical Properties

- (A) Reactions due to -OH group:
- (i) Acidic Nature: Phenol is a weak acid. The acidic nature of phenol is due to the formation of stable phenoxide ion in solution. The phenoxide ion is stable due to resonance. The negative charge is spread through out the benzene ring which is stabilising factor in the phenoxide ion. Electron withdrawing groups (-NO₂, -Cl) increase the acidity of phenol while electron releasing groups (-CH₃ etc.) decrease the acidity of phenol.

$$C_6H_5OH + H_2O \rightleftharpoons C_6H_5\overset{\Theta}{O} + H_3\overset{\Theta}{O}$$

Phenol is stronger acid than alcohols but weaker than the carboxylic acids and even carbonic acid.

GOLDEN KEY POINTS

- The acidic nature of phenol is observed as the following:
 - (i) Phenol changes blue litmus to red.
 - (ii) Highly electro positive metals react with phenol.

$$2C_6H_5OH + 2Na \longrightarrow 2C_6H_5ONa + H_2$$



(iii) Phenol reacts with strong alkalies to form phenoxides.

$$C_6H_5OH + NaOH \longrightarrow C_6H_5 \overset{\Theta}{O} \overset{\oplus}{N}a + H_2O$$

(iv) However phenol does not decompose Na₂CO₃ or NaHCO₃ because phenol is weaker acid than carbonic acid.

$$C_6H_5OH + Na_2CO_3$$
 or $NaHCO_3$ — No reaction

Ph—OH + NaHCO
$$_3$$
 $\stackrel{\longrightarrow}{\longleftarrow}$ Ph—ONa + H $_2$ CO $_3$ Acid-I Base-II Acid-II

$$\left. \begin{array}{l} Acid-I < Acid-II \\ Base-I < Base-II \end{array} \right\} Reaction \ in \ reverse \ direction \ .$$

Note: Acetic acid reacts with NaHCO₃ and gives effervescence of CO₂.

$$CH_3-C-OH + NaHCO_3$$
 \longrightarrow $CH_3-C-ONa$ $+$ H_2CO_3 $[H_2O + CO_2\uparrow]$ 0

(ii) Reaction with PCl₅: Phenol reacts with PCl₅ to form chloro benzene. POCl₃ formed as biproduct reacts with phenol to form triphenyl phosphate.

$$C_6H_5OH + PCl_5$$
 $\xrightarrow{\Delta}$ $C_6H_5Cl + POCl_3 + HCl$ $3C_6H_5OH + POCl_3$ \longrightarrow $(C_6H_5)_3PO_4 + 3HCl$

(iii) Reaction with Zn dust: When phenol is distilled with zinc dust benzene is obtained.

$$C_6H_5OH + Zn$$
 $\xrightarrow{\Delta}$ $C_6H_6 + ZnO$

—— Illustrations ——

Illustration 4. In which of the following compound deoxygenation is possible when heated with Zn

(I)
$$CH_2OH$$
 (II) CH_3OH (III) CH_3OH (III) CH_2OH (IV) $COOH$ (IV) $COOH$

Solution

Ans.(3) Observed in phenolic compound.

(iv) Reaction with NH₃: Phenol reacts with NH₃ in presence of anhydrous ZnCl₂ to form aniline.

(4) II, III

(v) Reaction with FeCl₃: Phenol gives violet colouration with FeCl₃ solution (neutral) due to formation of a complex.

$$C_6H_5OH + FeCl_3 \longrightarrow Violet colour$$

This reaction is used to differentiate phenol from alcohols.

(vi) Acetylation: Phenol reacts with acid chlorides or acid anhydrides in alkali solution to form phenyl esters.

$$C_6H_5OH + CICOCH_3 \xrightarrow{NaOH - HCl} C_6H_5O - C - CH_3$$

(vii) Benzoylation (Schotten-Baumann reaction)

$$C_6H_5OH + Cl$$
— C_6H_5 \xrightarrow{NaOH} C_6H_5O — C — C_6H_5 \parallel O

- **(B) Reaction of Benzene Ring :** The —OH group is ortho and para directing. It activates the benzene ring.
- (i) Halogenation: Phenol reacts with bromine in CCl₄ to form mixture of o-and p-bromo phenol.

$$\begin{array}{c|c}
OH & OH \\
\hline
OH & OH \\
\hline
OH & OH \\
\hline
Iow. temp.
\end{array}$$

$$+ OH \\
Br \\
Br \\
(Major)$$

Phenol reacts with bromine water to form a white ppt. of 2,4,6-tribromo phenol. (Test for phenol)

$$\begin{array}{c}
OH \\
OH \\
+ 3Br_2
\end{array}
\xrightarrow{H_2O}
\xrightarrow{Br}
\xrightarrow{Br}
\xrightarrow{Br}
+ 3HBr$$

(ii) Nitration: Phenol reacts with dil. HNO₃ at 0°-10°C to form o- and p- nitro phenols.

$$\begin{array}{c}
OH \\
& \text{dil.HNO}_3 \\
\hline
& 0-10^{\circ}C
\end{array}$$

$$\begin{array}{c}
OH \\
& NO_2 \\
& NO_3
\end{array}$$

When phenol is treated with nitrating mixture than it forms 2,4,6- trinitro phenol (picric acid) but it is not good method to form picric acid because nitric acid oxidise phenol into p-Benzoquinone

$$\begin{array}{c}
OH \\
\hline
Conc.HNO_3 \\
\hline
Conc.H_2SO_4
\end{array}$$

$$\begin{array}{c}
OH \\
NO_2
\end{array}$$

$$\begin{array}{c}
OH \\
NO_2
\end{array}$$

$$\begin{array}{c}
(2, 4, 6-Trinitrophenol (Picric acid)) \\
NO_2
\end{array}$$

(iii) Sulphonation: Phenol reacts with fuming H₂SO₄ to form o-and p-hydroxy benzene sulphonic acid at different temperatures.

OH
$$OH \longrightarrow OH \longrightarrow SO_3H$$

$$OH \longrightarrow OH \longrightarrow OH \longrightarrow OH \longrightarrow OH \longrightarrow SO_3H$$



(iv) Friedel - Craft 's reaction:

(v) Gattermann aldehyde synthesis: When phenol is treated with liquid HCN and HCl gas in presence of anhydrous AlCl₃ it yields mainly p-hydroxy benzaldehyde (formylation)

(vi) Reimer-Tiemann reaction: Phenol on refluxing with chloroform and NaOH (aqueous) followed by acid hydrolysis yields o-hydroxy benzaldehyde. When CCl₄ is used salicylic acid is formed.

$$\begin{array}{c|c} \text{CHCl}_3 & \text{ONa} & \text{NaOH} & \text{ONa} & \text{H}^+ & \text{OH} \\ \hline \text{OH} & \text{CHOl}_2 & \text{CHO} & \text{CHO} & \text{Salicylaldehyde} \\ \hline \\ \text{CCl}_4 & \text{ONa} & \text{ONa} & \text{ONa} & \text{OH} \\ \hline \text{60°C NaOH (aq.)} & \text{ONa} & \text{ONa} & \text{OH} \\ \hline \\ \text{CCOONa} & \text{NaOH} & \text{COOH} \\ \hline \end{array}$$

(vii) Kolbe's Schmidt reaction: It involves the reaction of C_6H_5OH with CO_2 and NaOH at 140° C followed by acidification to form salicylic acid.

$$OH \longrightarrow ONa \longrightarrow OH$$

$$COONa \longrightarrow COOH$$

$$Sodium salicylate \longrightarrow Salicylic acid$$

(viii) Hydrogenation: Phenol when hydrogenated in presence of Ni at 150-200°C forms cyclohexanol.

$$OH \qquad OH \qquad CH \qquad OH$$

$$OH \qquad CH \qquad OH$$

$$OH \qquad CH \qquad OH$$

$$CH \qquad OH \qquad OH$$

$$CH_2 \qquad OH \qquad OH$$

$$CH_2 \qquad OH \qquad OH$$

Cyclohexanol. (C₆H₁₁OH) (used as a good solvent)



(ix) Fries rearrangement reaction:

$$\begin{array}{c} C_{6}H_{5}OH+CH_{3}COCl & \xrightarrow{Pyridine} & C_{6}H_{5}OCOCH_{3} \\ \\ Phenyl \ Acetate \\ \\ C_{6}H_{5}OCOCH_{3} & \xrightarrow{anhydrous\ AlCl_{3}} \\ \\ Phenyl \ acetate \ (ester) & & & & & & \\ \end{array}$$

(x) Coupling reactions: Phenol couples with benzene diazonium chloride in presence of an alkaline solution to form a dye (p- hydroxy azobenzene) orange dye.

$$OH \xrightarrow{NaOH} OH \xrightarrow{NaOH} OH$$
 $OH \xrightarrow{NaOH} OH$
 $OH \xrightarrow{NaOH} OH$
 $OH \xrightarrow{NaOH} OH$
 $OH \xrightarrow{NaOH} OH$
 $OH \xrightarrow{NaOH} OH$

Phenol couples with phthalic anhydride in presence of conc. H_2SO_4 to form a dye (phenolphthalein) used as an indicator.

$$O = C C \stackrel{\downarrow}{=} O H \longrightarrow OH$$

$$O = C C \stackrel{\downarrow}{=} O H \longrightarrow OH \longrightarrow OH \longrightarrow OH$$

$$O = C C \longrightarrow OH \longrightarrow OH$$

Phthalic anhydride Phenol (2 molecules) Phenolphthalein (Colourless in acidic medium and pink in alkaline medium)

(xi) Lederer Manasse (Condensation with formaldehyde): Phenol condenses with HCHO (excess) in presence of NaOH or weak acid (H^{\dagger}) to form a polymer known as bakelite (resin).

Polymer bakelite (Phenol formaldehyde resin)



(xii) Reaction with acetone: (Condensation with acetone)

$$\begin{array}{c|c} OH & OH \\ \hline \\ OH & OH \\ \hline \\ H & H \\ \hline \\ O & CH_3-C-CH_3 \\ \hline \\ Bis - Phenol-A \\ p-p'- Isopropylidene diphenol \\ \hline \\ CH_3-C-CH_3 \\$$

(xiii) Oxidation:

Air
$$[O]$$
 CrO_2Cl_2
 $O + H_2O$ p-Benzoquionone (Pink)

(Phenol

(Phenol

(Elb's persulphate reaction)

Benzene-1, 4-diol

BEGINNER'S BOX-3

- 1. Reimer-Tiemann formylation reaction involves addition of :-
 - (1) Chloroform on phenoxide ion
- (2) Trichloromethyl carbanion on phenoxide ion
- (3) Dichlorocarbene on phenoxide ion
- (4) Hydroxide ion on phenol
- 2. Phenol reacts with benzenediazonium chloride solution to form a compound of the structure :-

(1)
$$HO \longrightarrow N=N \longrightarrow Cl$$

(2)
$$N=N-OH$$

$$(3) \bigcirc \longrightarrow N \longrightarrow N \longrightarrow OHC$$

$$(4) \bigcirc N = N - \bigcirc C$$

3. Phenol $\xrightarrow[\text{conc.H}_2\text{SO}_4]{\text{NaOH}}$ Green colour $\xrightarrow{\text{H}_2\text{O}}$ red colour $\xrightarrow{\text{NaOH}}$ Blue colour

This reaction is associated with the name of :-

- (1) Gattermann
- (2) Hofmann
- (3) Liebermann
- (4) Reimer-Tiemann

Test of Phenol:

- (1) Phenol turns blue litmus to red.
- (2) Aqueous solution of phenol gives a violet colour with a drop of ferric chloride.
- (3) Phenol gives Liebermann's nitroso test.
- (4) Aqueous solution of phenol gives a white ppt. of 2,4,6-tribromophenol with bromine water.
- (5) Phenol combines with phthalic anhydride in presence of conc. H_2SO_4 to form phenolphthalein which gives pink colour with alkali.



Differences between phenol and alcohol (C₂H₅OH):

- (1) Phenol is more acidic than aliphatic alcohol due to resonance in phenoxide ion.
- (2) Phenol gives violet colour with FeCl₃ while aliphatic alcohol does not give.
- (3) Phenol gives triphenyl phosphate with PCl₅ while aliphatic alcohol does not.
- (4) Phenol on oxidation gives quinone while alcohol gives aldehyde or ketone and acids.

Uses of Phenol:

Phenol is used:

- (1) As an antiseptic in soaps and lotions. "Dettol" (mixture of chloroxylenol and terpineol)
- (2) In manufacture of azodyes, phenolphthalein, picric acid (explosive), cyclohexanol (Solvent for rubber), plastics (bakelite) etc.
- (3) In manufacture of drugs like aspirin, salol, phenacetin etc.
- (4) As preservative for ink.

5.0 ETHER

R—O—R (Dialkyl ether), alkoxy alkane. It's General formula is $C_nH_{2n+2}O$.

CH₃—O—CH₂CH₃ (Methoxy ethane) or Ethyl methyl ether

Ether is monoalkyl derivative of R-OH and dialkyl derivative of H₂O

$$R-OH$$
 $\xrightarrow{-H}$ $R-O-R$ $\leftarrow \begin{array}{c} -2H \\ +2R \end{array}$ $H-O-H$

Classification: They may be classified as:

- (a) Simple or symmetrical ether. e.g. R-O-R
- (b) Mixed or unsymmetrical ether e.g. R-O-R'

Structure:

Bond σ 110° R Sp³hybridized

The molecule of ether is bent due to presence of lone pair.

The bond angle is 110°. It is greater than that of water (105°) due to the repulsion between bulkier alkyl groups. Due to bent structure, it possess dipole moment and hence are polar molecules.

5.1 General Methods of Preparation

- (a) From alkyl halides:
 - (i) By Williamson's synthesis:

$$R$$
— X + NaO — R — \longrightarrow R — O — R + NaX [SN^2 Reaction]

Ex.
$$CH_3$$
— CH_2 — $Cl + CH_3$ — ONa — CH_3 — CH_2O — CH_3 + NaC

Ex.
$$CH_3$$
 CH_2 $||$ $||$ CH_3 CH_3

Ex.
$$CH_2=CH-Cl + CH_3CH_2-ONa$$
 — No reaction [Stable by Resonance]



(ii) Reaction with Dry Ag₂O :
$$2RX + Ag_2O \xrightarrow{\Delta} R - O - R + 2AgX$$

Ex.
$$2CH_3$$
— CH_2 — $Cl + Ag_2O$ $\xrightarrow{\Delta}$ $CH_3CH_2OCH_2CH_3 + 2AgCl$

(b) From R-OH:

(i) By Bimolecular dehydration : $R-OH \xrightarrow{Con. H_2SO_4} R-O-R$

Mechanism:

$$R - \stackrel{\circ}{\text{O}} - H \xrightarrow{H^{\oplus}} \stackrel{\circ}{R} = \stackrel{\circ}{\text{O}} \stackrel{H}{\xrightarrow{-H_2O}} - R \xrightarrow{R - \stackrel{\circ}{\text{O}} - H} R \xrightarrow{-H^{\oplus}} R - O - R$$

$$CH_{3}CH_{2}-O-CH_{2}CH_{3} \stackrel{250^{\circ}C}{\longleftarrow} \underbrace{Al_{2}O_{3}-CH_{3}-CH_{2}-OH} \stackrel{conc.\ H_{2}SO_{4}}{\longleftarrow} \underbrace{CH_{3}CH_{2}-O-CH_{2}CH_{3}} \stackrel{(Williamson's\ continuous\ ether\ synthesis)}{\longleftarrow} \underbrace{CH_{2}=CH_{2}} \stackrel{350^{\circ}C}{\longleftarrow} \underbrace{CH_{2}=CH_{2}} \stackrel{(Elimination)}{\longleftarrow} \underbrace{CH_{2}=CH_{2}} \stackrel{(Elimination)}{\longleftarrow} \underbrace{CH_{3}CH_{2}-O-CH_{2}CH_{3}} \stackrel{(Williamson's\ continuous\ ether\ synthesis)}{\longleftarrow} \underbrace{CH_{2}=CH_{2}} \stackrel{(Elimination)}{\longleftarrow} \underbrace{CH_{2}=$$

(ii) Reaction with CH₂N₂ (diazomethane):

$$R$$
—OH + CH_2N_2 $\xrightarrow{\Delta}$ R —O— CH_2 —H + N_2

5.2 Physical Properties

- (i) CH₃OCH₃, CH₃OCH₂CH₃ are gases and higher ethers are volatile liquids.
- (ii) Ether are less polar.
- (iii) Ethers are less soluble in H_2O .
- (iv) Ethers have less BP then corresponding alcohol.

Illustrations -

Illustration 5. Ethers are less soluble in H₂O . Why?

Solution. Due to less polarity, it forms weaker H–Bonding with H₂O.

5.3 Chemical properties

Ethers are less polar so less reactive and do not react with active metals [Na,K], cold dil. acid, oxidising and reducing agent. They do not have any active functional group.

(1) **Basic nature :** Due to presence of ℓ .p on oxygen atom ether behave as lewis base

Ethers react with cold conc. acid and form oxonium salts.

Ex.
$$C_2H_5\ddot{\mathbf{C}}C_2H_5 \xrightarrow{\text{cold}\ ; \ \text{conc. HCl.}} \begin{bmatrix} C_2H_5 - \overset{\oplus}{\mathbf{O}} - C_2H_5 \\ H \end{bmatrix} Cl^{\circ}$$
 (diethyl oxonium chloride)



Ex.
$$C_2H_5$$
— \ddot{Q} — C_2H_5 $\xrightarrow{\text{cold ; conc.}}$ H_2SO_4 C_2H_5 — $\overset{\oplus}{O}$ — C_2H_5 H_5 C_2H_5 C_2H_5 C_2H_5 C_3 (diethyl oxonium hydrogen sulphate)

Ethers form dative bond with Lewis acids like BF_3 , $AlCl_3$, RMgX etc.

Ex.
$$R \longrightarrow B \longrightarrow F F F F F F R \longrightarrow R \longrightarrow R$$
 [Ether is used as a solvent] for Grignard reagent.

(2) Formation of peroxides: Ether add up atmospheric oxygen or ozonised oxygen. It is explained by Free radical mechanism as intermediate is free radical.

$$\begin{array}{cccc} C_2H_5 & \xrightarrow{O_2(\text{nonpolar})} & \text{CH}_3\text{CH}_2 & \text{O-CHCH}_3\\ & & \text{sunlight or UV} & \text{O-O-H} \\ \\ C_2H_5 \ddot{\mathbb{C}} C_2H_5 + : \ddot{\mathbb{C}} & \xrightarrow{C_2}H_5 \ddot{\mathbb{C}} C_2H_5 \text{ or } (C_2H_5)_2\text{O} & \xrightarrow{\bullet} \text{O} \\ & & \vdots \ddot{\mathbb{C}} \vdots & \\ \end{array}$$

$$CH_{3}CH_{2}-O-CH_{2}-Ph\xrightarrow{O_{2}}CH_{3}-CH_{2}-O-CH-Ph\xrightarrow{O_{2}}CH_{3}-CH_{2}-O-CH-Ph$$

Peroxides are unstable and explosives.

GOLDEN KEY POINTS

Test for peroxides

Ether (peroxide)
$$FeSO_4/KCNS$$
 Red colour

Ether (peroxides) + Fe^{+2} Fe^{+3} CNS^{\odot} Fe(CNS)₃ (Red)

- (3) Reaction with PCl_5 : ROR + $PCl_5 \xrightarrow{heat} 2RCl + POCl_3$
- (4) Reduction: $CH_3CH_2OCH_2CH_3 \xrightarrow{\text{Red P} + \text{HI}} 2CH_3CH_3$
- (5) Reaction with HX: $R-O-R'+HI \longrightarrow R-OH+R'-I$

Uses of ether:

- (i) General anaesthetic agent.
- (ii) Solvent for oil, fats, resins, Grignard reagent.
- (iii) For providing inert & moist free medium to organic reaction e.g. Wurtz reactions.
- (iv) In perfumery.
- (v) Di-isopropyl ether In petrol as an antiknock compound.
- (vi) Mixture of alcohol and ether is used as a substitute of petrol. Trade name "Natalite"



6.0 CARBONYL COMPOUNDS

Organic Compounds having >C = O group are called carbonyl compounds and >C = O group is known as carbonyl group. It's general formula is C_n H_{2n} O (n = 1, 2, 3......) Carbonyl compounds are grouped into two categories.

(a) Aldehydes: Aldehyde group is -C-H (also known as formyl group). It is a monovalent group

Carbon atom of C - H group is of 1° nature i.e. $R - \overset{1^\circ}{C} = O$

(b) Ketones : The carbonyl group >C = O is a Ketonic group when its both the valencies are satisfied by alkyl group. It is a bivalent group.

Carbon atom of >C = O group is of 2° nature i.e. R > C = O

Ketones are further classified as :

- (i) Simple or Symmetrical ketones: Having two similar alkyl groups. R > C = O
- (ii) **Mixed or unsymmetrical ketones**: Having two different alkyl groups. $\frac{R}{R'} > C = O$

Ex. (Ketones): Symmetrical Unsymmetrical

$$CH_3$$
 $C = O$ CH_3CH_2 CH_3 $C = O$

(Acetone or Dimethyl ketone) (Ethyl methyl ketone)

Propanone Butanone

In all the compounds given above, lone pair of electrons and double bond are in conjugate system.

 $\begin{pmatrix} C \\ -C \end{pmatrix}$ so resonance occurs. These compounds have -C – group still they are not carbonyl compounds

because these compounds have characteristic reactions different from carbonyl compounds.

Structure : In >C = O compounds C-atom is sp² hybridised which forms two σ bonds and one π bond. The unhybridised atomic orbital of C-atom and the parallel 2p orbital of oxygen forms the π bond in >C = O group



Due to electro-negativity difference in C & O atoms, the >C = O group is polar.

 $>_C^{\delta^+} = \stackrel{\delta^-}{O}$ Hence aldehydes and Ketones possess considerable dipole moment.

General Methods of Preparation 6.1

- (A) For both Aldehydes and Ketones
- (1) By Oxidation of Alcohols:
 - Oxidation of primary alcohols gives aldehyde and oxidation of (a) By $K_2Cr_2O_7 / H_2SO_4$: secondary alcohols gives Ketones.

$$RCH_2OH \xrightarrow{[O]} RCHO \text{ (Aldehyde)}$$

Aldehydes are quite susceptible to further oxidation to acids -

$$RCH_2OH \xrightarrow{[O]} R-CHO \xrightarrow{[O]} R-COOH$$

Thus oxidation of primary alcohols is made at the temperature much above the boiling point of aldehyde and thus aldehydes are vapourised out and prevented from being oxidised.

(b) Mild Oxidising Agent: 1° alcohols will get oxidised with CrO₃ / Pyridine, (collin's reagent) or P.C.C (Pyridinium chloro chromate $CrO_3 + C_5H_5N + HCI$) to aldehyde and 2° alcohols to ketone.

$$RCH_2OH + [O] \longrightarrow RCHO + H_2O$$

By this reaction, **good yield of aldehyde** is possible.

(2) Dehydrogenation of alcohols:



(3) By dry distillation of Ca-salts of carboxylic acid:

Calcium alkanoate

Calcium formate

(
$$R$$
- C - R and HCHO are also formed) \parallel O

$$\begin{array}{ccc}
R \boxed{COO} & & & & & R \\
RCO \boxed{O} & & & & & & R
\end{array}$$

$$C = O + CaCO_3$$

Calcium-alkanoate

Ketone

Calcium salts of acids other than formic acid on heating together give unsymmetrical ketone

To prepare ethyl methyl ketone Calcium acetate and Calcium propionate are used :

$$CH_{3} CO Ca + Ca CO C CH_{2}CH_{3}$$

$$CH_{3} CO Ca + Ca CO CH_{2}CH_{3}$$

$$CH_{3} CO Ca + Ca CO CH_{2}CH_{3}$$

$$CH_{3} CO Ca + Ca CO CH_{2}CH_{3}$$

$$CH_{3} C = O + 2CaCO_{3}$$

Calcium Acetate Calcium propionate

Ethyl methyl ketone

(4) By Thermal decomposition of carboxylic acids : Vapour of carboxylic acids when passed over MnO/300°C give carbonyl compounds



(5) By Hydrolysis of gem dihalides: Terminal gem-dihalides on hydrolysis give aldehydes while the non-terminal gem-dihalides give ketones.

$$CH_{3}CH \stackrel{Cl}{\stackrel{KOH(aq)}{\frown}} [CH_{3}CH \stackrel{O}{\stackrel{H}{\frown}}] \quad \stackrel{-H_{2}O}{\longrightarrow} \quad CH_{3}CHO$$

Terminal gem-dihalide [unstable]

$$\begin{array}{c} \text{Cl} & \text{CH}_3 - \text{C} - \text{CH}_3 & \xrightarrow{\text{KOH(aq)}} & \begin{bmatrix} \text{OH} \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \text{OH} \end{bmatrix} \xrightarrow{-\text{H}_2\text{O}} & \text{CH}_3 - \text{C} - \text{CH}_3 \\ \text{Acetone} & \text{OH} \\ \end{bmatrix}$$

(6) By Oxidation of diols: With periodic acid (HIO₄) or lead tetra acetate (CH₃COO)₄ Pb vicinal diols get oxidised to form carbonyl compounds

(7) By Ozonolysis of alkenes: This reaction is used to determine the position of double bond in alkene. Zn is used to decompose H₂O₂ formed during hydrolysis.

$$RCH=CH_{2}+O_{3} \longrightarrow RCH \longrightarrow RCH \longrightarrow RCH \longrightarrow RCHO + HCHO$$

$$Ozonide$$

$$R-C=CH_{2}+O_{3} \longrightarrow R-C \longrightarrow R-C \longrightarrow R-C \longrightarrow R-C+O+HCHO$$

$$R \longrightarrow R-C=CH_{2}+O_{3} \longrightarrow R-C \longrightarrow R-C \longrightarrow R-C+O+HCHO$$

- (8) From Alkyne:
 - (a) Hydration: With dil $H_2SO_4 \& 1\% HgSO_4$ at $60-80^{\circ}C$.

$$CH = CH + H_2O \xrightarrow{H_2SO_4} [CH_2 = CHOH] \xrightarrow{Tautomerisation} CH_3 \xrightarrow{C} H$$

Other alkynes mainly give ketone:

$$CH_{3}C \stackrel{\frown}{=} CH + H_{2}O \xrightarrow{H_{2}SO_{4} \atop Hg^{+2}} CH_{3} \xrightarrow{C=CH_{2}} CH_{2} \xrightarrow{Tautomerism} CH_{3} \xrightarrow{C} CH_{3}$$

$$OH \atop (enol)$$



(b) Hydroboration : Reaction with B₂H₆ or R₂BH give alkenyl dialkyl borane.

$$R-C \stackrel{f}{=} CH + R_2BH \longrightarrow R-CH = CHBR_2 \xrightarrow{H_2O_2} RCH = CHOH \xrightarrow{\text{Tautomerism}} R-CH_2-C-H + R_2BOH$$

$$CH_{3}-C \equiv C-CH_{3} + R_{2}BH \longrightarrow CH_{3}-CH=C-CH_{3} \xrightarrow{H_{2}O_{2}} OH^{-}$$

$$BR_{2}$$

- (B) For Aldehydes only
- (1) Rosenmund's reduction:

 ${\rm BaSO_4}$ controls the further reduction of aldehyde to alcohols. Formaldehyde can not be prepared by this method.

$$\begin{array}{ccc} \textbf{Ex.} & & C_2 \textbf{H}_5 \textbf{COCl} + \textbf{H}_2 & \xrightarrow{& \textbf{Pd/BaSO}_4 \ \\ & \textbf{Propionyl Chloride} & & \textbf{Propanal} \end{array}$$

(2) Stephen's reduction:

- (C) For Ketones only
- (1) From Grignard's reagent:

$$RMgX + R - C = N \longrightarrow R - C = NMgX \xrightarrow{2H_2O} R - C = O + NH_3 + Mg \xrightarrow{X} OH$$

$$RMgX + R - C - CI \longrightarrow R - C - R$$

$$(Limited)$$

$$RMgX + R - C - OR \xrightarrow{\Delta} R - C - R + ROMgX$$

$$(Limited)$$

(2) From dialkyl Cadmium: R'CdR' (dialkyl Cadmium) is an organometallic compound.

$$RCOCl + R'CdR' \longrightarrow RCOR' + R'CdCl$$

This reaction is superior than Grignard Reaction because the ketones formed, further reacts with Grignard reagent to form 3° alcohols.

Ex.
$$CH_3COCI + C_2H_5 Cd \longrightarrow CH_3 C = O + C_2H_5 Cd$$

6.2 Physical Properties

State : Only formaldehyde is gas, all other carbonyl compounds upto C_{11} are liquids and C_{12} & onwards solid.

Solubility: C_1 to C_3 (formaldehyde, acetaldehyde and propionaldehyde) and acetone are freely soluble in water due to polarity of $> \stackrel{\delta^+}{C} = \stackrel{\delta^-}{O}$ bond and can form H—bond with water molecule. C_5 onwards are insoluble in water.

H-bonding

Boiling point : Boiling point ∞ Molecular weight

Boiling point order is - Alcohol > Ketone > Aldehydes > Alkane (of comparable molecular mass)

This is because in alcohols intermolecular H-bonding is present but in carbonyl compounds H-bonding doesn't exist, instead dipole-dipole & vander waal force of attraction is present. Alkanes are non polar.

$$>$$
 $\stackrel{\delta^+}{C} = \stackrel{\delta^-}{O} - \cdots - \stackrel{\delta^+}{C} = \stackrel{\delta^-}{O}$

Density: Density of carbonyl compounds is lower than water.

BEGINNER'S BOX-4

- 1. Acids do not give the characteristic reactions of C=O group because of :-
 - (1) Dimerisation

(2) Resonance

(3) Cyclic structures

- (4) Attached alkyl radical
- 2. The vapour density of a compound is 44. Its molecular formula will be -
 - $(1) C_2H_5O$
- $(2) C_2H_4O_3$
- (3) $C_4H_{10}O$
- $(4) C_5 H_{12} O$

- **3.** 23 gm of sodium of reaction with methyl alcohol gives :
 - (1) Half mole of H₂
- (2) One mole of H₂
- (3) One mole of O_2
- (4) none

6.3 Chemical Properties

Carbonyl compounds undergo following reactions:

- **6.3.1 Nucleophilic addition reactions** (Already discussed in Reaction Mechanism Part-2)
- 6.3.2 Other reactions
- 6.3.3 Reactions of only aldehyde
- 6.3.4 Reactions of only ketones



6.3.2 Other reactions

(a) Reduction: The nature of product depends upon the reducing agent used.

(i)
$$C = O \longrightarrow CH_2$$

Reducing agents are

- Red P/HI at 150℃
- Zn-Hg/HCl [Clemmensen's reduction]
- (i) N₂H₄ (ii) $\overset{\circ}{O}$ H / Δ [Wolff Kishner reduction]



>CHOH | Reducing agents are

- Metal + H_o
- LiAlH₄
- NaBH₄
- Na + C₂H₅OH

(b) Reaction with PCl₅ & SOCl₂:

Phosphorus penta chloride

$$>$$
C = O + SOCl₂ \longrightarrow $>$ C $<$ Cl + SO₂

Thionyl chloride

(c) Aldol Condensation: Carbonyl compounds which contain α-H atoms undergo condensation with dil. NaOH to give aldol. Aldol contains both alcoholic and carbonyl group, which on heating in alkaline medium gets converted into α , β -unsaturated carbonyl compound.

Mechanism of aldol condensation: It takes place in the following two stages:

- Formation of Carbanion
- (ii) Combination of carbanion with other carbonyl molecule.
- (i) Formation of Carbanion : α -H atom of $\sum_{i=0}^{\infty} C_i = 0$ group are quite acidic which can be removed easily as proton, by a base

Carbanion thus formed is stable because of resonance -

$$\overset{\circ}{C}H_{2} \xrightarrow{C} C \longrightarrow CH_{2} = C \longrightarrow H$$



(ii) Combination of carbanion with other carbonyl molecule:

$$\begin{array}{c} O \\ CH_3-C+CH_2-C=O \end{array} \longrightarrow \begin{array}{c} CH_3-C-CH_2-CHO \\ H \end{array}$$

$$\begin{array}{c} CH_3-C-CH_2-CHO \\ H \end{array}$$

$$\begin{array}{c} Aldehyde \\ (other molecule) \end{array}$$

$$\begin{array}{c} O \\ H_2O \\ OH \\ CH_3-C-CH_2-C=O \end{array} \longrightarrow \begin{array}{c} O \\ OH \\ Aldol \end{array}$$

$$\begin{array}{c} O \\ OH \\ CH_3-CH=CH-CH \\ \alpha,\beta-Unsaturated aldehyde \end{array}$$

$$\begin{array}{c} O \\ OH \\ Aldol \end{array}$$

Identical carbonyl compounds — Simple or self aldol condensation.

Different carbonyl compounds ——— Mixed or crossed aldol condensation.

Simple or Self condensation:

$$\begin{array}{c} \text{CH}_3 - \text{C} - \text{CH}_3 + \text{H} - \text{CH}_2 - \text{C} - \text{CH}_3 & \longrightarrow \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{C} & \longrightarrow \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{C} & \longrightarrow \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{C} & \longrightarrow \\ \text{Mesityl oxide or} \\ \text{OH} & \text{CH}_3 & \text{Mesityl pent} - \text{3-en-} \text{2-one} \\ \end{array}$$

Mixed or Crossed aldol Condensation:

$$\begin{array}{cccc} CH_{3}CH + CH_{3}-C-CH_{3} & \xrightarrow{Weak} Total \ (4) \ products & & \\ \parallel & \parallel & \parallel & \\ O & O & & \\ \end{array}$$

Mixed aldol condensation products of the above reaction are :

$$\begin{array}{c} CH_3 \\ \downarrow \alpha \\ CH_3-C+CH_2-CHO \xrightarrow{OH} \stackrel{\Theta}{\longrightarrow} CH_3-C-CH_2-CHO \xrightarrow{\stackrel{\Theta}{\longrightarrow} H/\Delta} CH_3-C=CH-CHO \\ \downarrow OH \\ OH \\ (Aldol) \end{array}$$



Illustrations -

Illustration 6. CH₃CHO + CH₃CH₂CHO Total 4 products. Write structure of products?

Solution.

$$CH_3-CH_2-CH+CH_2-CHO \xrightarrow{\Theta_{OH}} (Aldol) \xrightarrow{O_{H/\Delta} \atop -H_2O} CH_3-CH_2-CH=CH-CHO$$

GOLDEN KEY POINTS

• If in crossed aldol condensation reaction , only one carbonyl compound have $\alpha-H$ then total two products are formed.

$$CH_3CHO + C_6H_5CHO$$
 $\xrightarrow{\Theta_{OH}}$ Total 2 product.

(Crotonaldehyde)

$$\begin{array}{cccc} C_6H_5-CH+\overset{\alpha}{C}H_2-CHO & \xrightarrow{\quad \Theta_{OH}} \text{(Aldol)} & \xrightarrow{\quad \Theta_{OH/\Delta}\\ \quad & \mid & \mid \\ \quad & O & H \end{array} \qquad \begin{array}{c} C_6H_5-CH=CH-CHO \end{array}$$

(Cinnamaldehyde)

• **Intramolecular** aldol condensation :

CH₃-C-CH₂-CH₂-C-CH₃
$$\xrightarrow{\theta_{OH}}$$
 CH₃-C-CH₂-CH₂-C- $\overset{\circ}{C}$ H₂ $\xrightarrow{\theta_{OH}}$ CH₃-C-CH₂-CH₂-C- $\overset{\circ}{C}$ H₃ $\xrightarrow{\theta_{OH}}$ $\xrightarrow{\theta_{OH}}$

Here one more product having 3 membered ring is also possible, but 5 membered ring is more stable than 3 membered ring so above product is formed as a major product.



(d) Oxidation reactions : Oxidation reactions :

(i) By K₂Cr₂O₇/H₂SO₄: On oxidation with K₂Cr₂O₇/H₂SO₄ 1° alc. gives aldehyde, which on further oxidation gives acid with same number of carbons. If 2° alcohol is oxidised at elevated temperature using KMnO₄/H[®], it gets oxidised to give acids with less number of C-atom.

$$\begin{array}{c} H_{3}C-CH_{2}OH \xrightarrow{[O]} H_{3}C-CH=O \xrightarrow{[O]} H_{3}C-COOH \\ (1^{\circ} alcohol, 2C) & (Acid with 2C-atoms) \\ \\ CH_{3}CH_{2}CH_{2}-CH-CH_{3} \xrightarrow{[O]} CH_{3}CH_{2}CH_{2}-C-CH_{3} \xrightarrow{[O]} CH_{3}CH_{2}COOH+CH_{3}COOH \\ OH & O & (Acid having less number of C) \\ (2^{\circ} alcohol, 5C) & (2^{\circ} alcohol, 5C) \end{array}$$

(ii) SeO₂ (Selenium dioxide): Ketones or aldehydes on oxidation with SeO₂ give dicarbonyl compounds. This reaction is possible only in compounds containing α -CH₂- unit.

HCHO doesn't show this reaction.

$$\overset{\alpha}{\text{CH}_3\text{CHO}} + \text{SeO}_2 \xrightarrow{\Delta} \text{H-C-C-H} + \text{Se} + \text{H}_2\text{O}$$
 $\parallel \parallel \parallel$
 O O
 Glyoxal
 $\text{CH}_3\text{-C-}\overset{\alpha}{\text{C}}\text{H}_3 + \text{SeO}_2 \xrightarrow{\Delta} \text{CH}_3\text{-C-C-H} + \text{Se} + \text{H}_2\text{O}$
 $\parallel \parallel \parallel$
 O O O
 $\text{Methyl glyoxal (Pyruvaldehyde)}$

6.3.3 Reactions of only aldehydes:

(a) Cannizaro's reaction: Those aldehydes which do not contain α -H atom give this reaction, with conc. NaOH or KOH; Products are Salt of carboxylic acid + alcohol

In this reaction one molecule of carbonyl compounds is oxidised to acid, while other is reduced to alcohol, such type of reactions are called redox reaction.

HCHO + HCHO
$$\xrightarrow{\text{Conc.}}$$
 HCOONa + CH₃OH

Mechanism involved in cannizaro's reaction:

(a) Rapid reversible addition of $\overline{O}H$ to one molecule of HCHO.

$$\begin{array}{c|c} & OH \\ H-C-H & \xrightarrow{\Theta_{OH}} & H-C-H \\ & & & \\ & & & \\ \end{array}$$



(b) Transfer of hydride ion H to second molecule of HCHO

$$\begin{array}{c|ccccc} OH & O & OH & O^{\circ} \\ \hline H-C-H & + C-H & - H-C+H-C-H \\ O & H & O & H \\ \hline \end{array}$$

(c) Proton exchange

When molecules are same ———Simple cannizaro reaction (disproportionation reaction) Two different molecules ——Mixed cannizaro reaction (Redox reaction)

In mixed or crossed cannizaro reaction more reactive aldehyde is oxidised and less reactive aldelyde is reduced.

(b) Tischenko reaction: It is a modified cannizaro reaction. All aldehydes undergo this reaction in presence of (C₂H₅O)₃Al, to form ester.

$$\begin{array}{ccc} \textbf{Ex.} & \text{CH}_{3}\text{CHO} + \text{CH}_{3}\text{CHO} & \xrightarrow{\text{(C}_{2}\text{H}_{5}\text{O)}_{3}\text{Al}} & \underbrace{\text{CH}_{3}\text{COOH} + \text{CH}_{3}\text{CH}_{2}\text{OH}}_{\text{Esterification}} \downarrow \\ & & & & \\ \hline \end{array}$$

(c) Reducing character: Aldehydes are easily oxidised so they are strong reducing agents.

Tollen's reagent: It oxidises aldehydes. Tollen's reagent is ammonical silver nitrate solution



(ii) Fehling's solution: It is a mixture of aqueous CuSO₄, NaOH and sodium potassium tartarate.

Fehling solution A- (aq.) solution of CuSO₄

Fehling solution B-Roschelle salt (Sodium potassium tartarate + NaOH)

Fehling solution A + Fehlings solution B(Dark blue colour of cupric tartarate)

$$RCHO + Cu^{+2} + \overset{\circ}{O}H \longrightarrow RCO\overset{\circ}{O} + Cu_2O$$

(Cuprous oxide-Red ppt.)

$$Cu^{2+}$$
 \longrightarrow Cu^{+}

(Cupric - Blue) (Cuprous - Red ppt.)

(iii) **Benedict's solution**: It is a mixture of CuSO₄ + sodium citrate + NaOH. It provides Cu⁺². It is reduced by aldehyde to give red ppt of cuprous oxide.

$$RCHO + Cu^{2+} + OH^{-} \longrightarrow RCO\overset{\circ}{O} + Cu_{2}O$$

(Cuprous oxide-Red ppt.)

(iv) Schiff's reagent : Dilute solution of p-rosaniline hydrochloride or magenta dye, is a pink coloured dye and is known as schiff' dye.

Its pink colour is discharged by passing SO_2 gas and the colourless solution obtained is called schiff's reagent, Aldehyde reacts with this reagent to restore the pink colour.

6.3.4 Reaction of Only Ketones

(1) **Reduction**: Acetone is reduced by magnesium amalgam and water to give pinacol.

$$CH_3$$
 $C=O+O=C$ CH_3 $Mg-Hg$ $CH_3-C-C-CH_3$ CH_3 C

(2) Reaction with chloroform:

$$CH_3$$
 $C=O + CHCl_3$ CH_3 CH_3 CH_3 CCl_3 CH_3 CCl_3 CH_3 CCl_3 CCl

(3) Oxidation reaction: According to popoff's rule C = O group stays with smaller alkyl group.

$$\begin{array}{c} O \\ \parallel \\ CH_3-CH_2-C-CH_3 \end{array} \xrightarrow{[O]} CH_3COOH + CH_3COOH \\ \end{array}$$



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BEGINNER'S BOX-5

- 1. The compounds capable in reaction with Tollen's reagent is (are):
 - (1) Formaldehyde
- (2) Formic acid
- (3) Acetaldehyde
- (4) All the above

2. Acetaldehyde reacts with NaOH to form :-

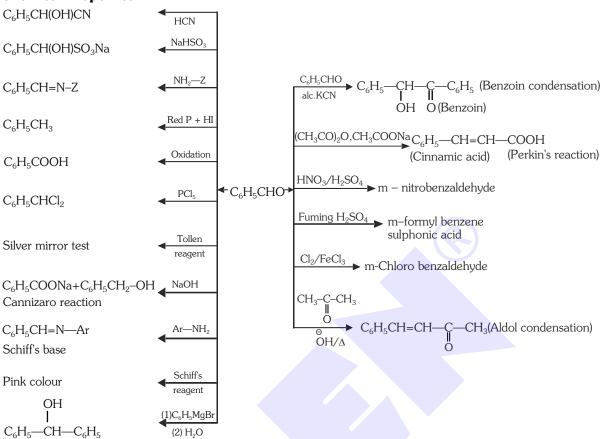
- 3. Fehling's solution is a :-
 - (1) Solution of magenta dye bleached by SO₂
 - (2) Ammonical solution of AgNO₃
 - (3) Mixture of a solution of CuSO₄ and a solution of caustic soda and sodium potassium tartarate
 - (4) Alcoholic solution of 2,4-dinitrophenylhydrazine

7.0 BENZALDEHYDE (C6H5CHO) [OIL OF BITTER ALMONDS (COMPONENT OF BITTER ALMOND)]

7.1 **General Methods of Preparation**



7.2 Chemical Properties



8.0 CARBOXYLIC ACID

Organic compounds having -COOH group are called Carboxylic acids. This functional group is composed of

O
$$\parallel$$
 Carbonyl ($-$ C $-$) and hydroxyl ($-$ OH) group.

Carbonyl group Hydroxyl group Carboxylic group

The properties of the carboxylic group are not simply the combined properties of these two groups, but it has its own distinctive properties. The acidic nature of carboxylic acids is due to the presence of replaceable H-atom in the Carboxylic group. The general formula is $C_nH_{2n}O_2$.

Classification:

Monocarboxylic acid (RCOOH): Having one carboxylic group, also called monobasic acid.

General formula - $C_nH_{2n}O_2$ ($n=1,\,2,\,3,\,\ldots$). Higher mono carboxylic acids are called **fatty acids**.

Ex. CH₃COOH acetic acid



Pre-Medical

Dicarboxylic acid: Having two carboxylic groups, also called dibasic acid.

Tricarboxylic acid: Having three carboxylic groups also called tribasic acid.

$$\operatorname{Ex.}$$
 $\operatorname{HO-C-COOH}$ Citric acid $\operatorname{CH_2COOH}$

Structure : The carbon atom of -COOH group is sp^2 hybridised, this C- atom is in centre and thus bond angle around C-atom is 120° .

8.1 General Methods of Preparation

8.1.1 By Oxidation of alcohols & carbonyl compounds : Oxidation is carried out by acidified $K_2Cr_2O_7$ or $KMnO_4$.

$$RCH_{2}OH \xrightarrow{[O]} RCHO \xrightarrow{[O]} RCOOH$$

Acids are third oxidation products of alkane.

GOLDEN KEY POINTS

- Aldehyde on oxidation give acids having same no. of C-atoms.
- Ketones on oxidation give acids having less no. of C-atoms.
- Oxidation of Ketones occurs on prolonged treatment with strong oxidising agent.
- 8.1.2 By hydrolysis of alkane nitriles or cyanides: Complete hydrolysis takes place in acidic medium (dil.

HCl). In alkaline medium there is partial hydrolysis.

$$R-C = N \xrightarrow{H_2O/H^{\oplus}} R-C = NH \xrightarrow{Tautomerism} R-C-NH_2 \xrightarrow{H_2O/H^{\oplus}} R-C-OH+NH_3$$

8.1.3 By alkaline hydrolysis of 1, 1, 1-trihaloalkane:

$$R-C \xrightarrow{Cl} Cl + 3KOH \xrightarrow{-3KCl} R-C \xrightarrow{OH} \xrightarrow{KOH} RCOOK + H_2O \xrightarrow{HCl} RCOOH + KCl$$



8.1.4 By hydrolysis of acid derivatives:

$$\begin{matrix} O & & O \\ \parallel & \parallel \\ R-C-Z+H-OH & \longrightarrow R-C-OH+HZ \end{matrix}$$

Reactivity order of acid derivatives:

$$RCOCl > (RCO)_2O > RCOOR > RCONH_2$$

$$RCOCl \xrightarrow{HOH \atop dil.\,acid} RCOOH + HCl$$

$$(RCO)_2O \xrightarrow{HOH} 2RCOOH$$

$$RCOOR' \xrightarrow{HOH} RCOOH + R'OH$$

$$R$$
— $CONH_2 \xrightarrow{HOH} RCOOH + NH_3$

8.1.5 From Grignard's reagent:

$$RMgX + O = C = O \longrightarrow R - C - OMgX \xrightarrow{H_2O} R - C - OH + Mg < X$$

Carbon dioxide

Solid CO₂(dry ice) is used

8.2 Physical Properties

Carboxylic acids from C_1 — C_4 are completely soluble in water.

Solubility
$$\propto \frac{1}{\text{molecular weight}}$$

Solubility is due to intermolecular H - bonding with water molecules.

Boiling point:

Acids > alcohol

This is because in acids two oxygen atoms take part in H - bonding (while in alcohol only one O - atom takes part).

In vapour or soluble state lower acids occur

in the form of dimers.

$$R-C$$
 $O-H-O$ $C-R$

But in liquid state it exists in polymer form.

Melting point: Acids having even number of C-atoms have higher melting point as compared to having odd number of C - atoms. The carboxyl group and terminal methyl group in even member acids lie on opposite side to provide more close packing in crystal lattice which results in high melting point.



Chemical Properties 8.3

8.3.1 Reaction due to - H atom of - COOH group

(a) Acidic character:

Carboxylate ion is stabilised by resonance so carboxylic acids show considerable acidic character.

In case of alcohol alkoxide ion is not stabilised so they are neutral.

$$R - OH \rightleftharpoons R - O^- + H^+$$

alkoxide ion

- (a) Carboxylic acids turn blue litmus to red.
- (b) Addition of carboxylic acid to NaHCO₃ in water gives out effervescence of CO₂.

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2 \uparrow$$

(c) Form salts with alkalies.

RCOOH + NaOH
$$\longrightarrow$$
 RCOONa + H₂O

$$RCOOH + Ca(OH)_2 \longrightarrow (RCOO)_2Ca + H_2O$$

(d) Action of metals.

RCOOH + Na
$$\longrightarrow$$
 RCOONa + $\frac{1}{2}H_2$

The acidic character order is:

Acidic character may be explained on the basis of I effect and resonance.

(b) Reaction with CH₂N₂: Methyl ester can be prepared by this method.

$$\begin{array}{ccc} RCOOH + CH_{2}N_{2} & \longrightarrow & RCOOCH_{3} + N_{2} \\ & & \\ Methyl \ ester \end{array}$$

8.3.2 Reaction due to - OH group

(a) Esterification:

$$CH_3COOH + HOC_2H_5 \xrightarrow{Conc.H_2SO_4} CH_3COOC_2H_5 + H_2O$$

(b) Reaction with NH₃:

$$CH_{3}COOH + NH_{3} \longrightarrow CH_{3}COONH_{4} \stackrel{\Delta}{\longrightarrow} CH_{3}CONH_{2} \stackrel{P_{2}O_{5}/\Delta}{\longrightarrow} CH_{3}CN$$

(c) Reaction with thionyl chloride:

$$CH_3COOH + SOCl_2 \xrightarrow{Pyridine} CH_3COCl + SO_2 \uparrow + HCl$$

(d) Reaction with PCl₅:

$$CH_3COOH + PCl_5$$
 \longrightarrow $CH_3COCl + POCl_3 + HCl_3$



(e) Reaction with P₂O₅ (dehydrating agent) :

$$\begin{array}{c|c} CH_3CO \overline{OH} & \xrightarrow{P_2O_5 \text{ or}} & CH_3CO \\ CH_3COO \overline{H} & \xrightarrow{conc. H_2SO_4\Delta} & CH_3CO \\ \end{array} > O \ + \ H_2O$$

HCOOH is dehydrated by Conc. H₂SO₄

$$\text{HCOOH} \xrightarrow{\text{Conc.H}_2\text{SO}_4} \text{CO} + [\text{H}_2\text{O.H}_2\text{SO}_4]$$

8.3.3 Reaction due to ${\overset{O}{\underset{-C}{\parallel}}}_{-C}$ group of COOH :

(a)
$$CH_3$$
— $COOH + 4H$ $\xrightarrow{LiAlH_4}$ $CH_3CH_2OH + H_2O$

(b) R—COOH +
$$3H_2$$
 $\xrightarrow{Ni/\Delta}$ R—CH₂—OH + H₂O

(c)
$$R - C - OH + 6HI$$
 $\xrightarrow{\text{Red P} \atop \text{\& high Pr}}$ $R - CH_3 + 2H_2O + 3I_2$

8.3.4 Reaction due to - COOH group:

(a) Decarboxylation:

$$CH_3COONa + NaOH / CaO$$

$$\xrightarrow{\Delta} CH_4 + Na_2CO_3$$
(soda lime)

(b) Kolbe's electrolysis:

$$\begin{array}{c} \text{CH}_3\text{COONa} \\ \text{CH}_3\text{COONa (aq.)} \end{array} \xrightarrow{\text{Electrolysis}} \begin{array}{c} \text{CH}_3 \\ \text{I} \\ \text{CH}_3 \end{array} + \text{CO}_2 + \text{NaOH} + \text{H}_2 \end{array}$$

(c) Hunsdiecker reaction:

$$CH_3COOAg + Br_2$$
 $\xrightarrow{CCl_4 \atop hv}$ $CH_3Br + AgBr + CO_2$ or Cl_2 or $CH_3Cl + AgCl + CO_2$

(d) Formation of carbonyl compounds:

$$(CH_3COO)_2Ca \xrightarrow{\Delta} CH_3COCH_3$$
 \longrightarrow Dry distillation $(HCOO)_2Ca \xrightarrow{\Delta} HCHO$

(e) Schmidt reaction: The amine formed has one C - atom less than the reactant acid.

$$RCOOH + N_3H \xrightarrow{\quad (1)H_2SO_4 \quad} RNH_2 + CO_2 + N_2$$

Hydrazoic acid



8.3.5 Reaction due to alkyl (R) group:

(a) Halogenation [HVZ reaction] : [Hell volhard Zelinsky reaction] : In this reaction α - H atoms are replaced by halogen atoms.

$$\text{CH}_3\text{COOH} + \text{Cl}_2 \xrightarrow{\quad P \quad} \text{CICH}_2\text{COOH} \xrightarrow{\quad P/\text{Cl}_2 \quad} \text{Cl}_2\text{CHCOOH} \xrightarrow{\quad P/\text{Cl}_2 \quad} \text{Cl}_3\text{CCOOH}$$

GOLDEN KEY POINTS

Test for HCOOH and CH₃COOH

Test	НСООН	CH ₃ COOH
1. Reducing character		
Reducing agents		
Tollen reagent	Silver mirror	×
Fehling solution	Cu ₂ O red ppt.	×
$K_2Cr_2O_7$	Cr ⁺³ (green)	×
2. Decarboxylation.	$Na_2CO_3 + H_2$	CH ₄

Uses of Formic Acid:

- (i) As an antiseptic
- (ii) For preservation of fruits.
- (iii) For leather tanning.
- (iv) In dying wool and cotton fabrics.

Uses of Acetic Acid:

- (i) Vinegar (6 10% solution) used as **table acid** and manufacture of pickles.
- (ii) For manufacture of rubber from latex and casein from milk CH₃COOH is used as coagulant.
- (iii) As a solvent and laboratory reagent.

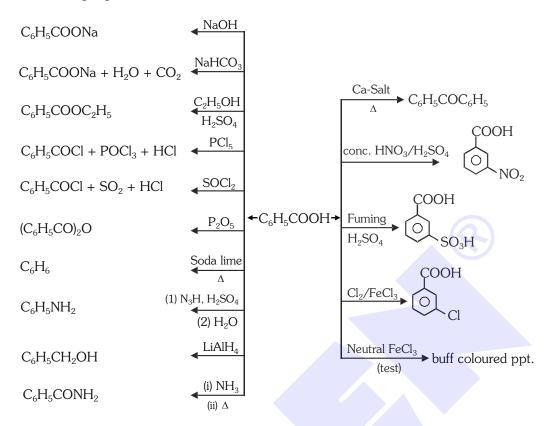
9.0 BENZOIC ACID (C₆H₅COOH)

9.1 General Method of Preparation:

C ₆ H ₅ CHO C ₆ H ₅ CH ₃	$[O]$ $H^{+}/KMnO_{4}$ $H_{2}O^{+}$	
C ₆ H ₅ CN C ₆ H ₅ CCl ₃	(i) aq. KOH (ii) H (i) CO ₂ (ii) H ₂ O	
C ₆ H ₅ MgBr H-O C ₆ H ₄ COOH (o, m, p)	Zn Δ	\longrightarrow C ₆ H ₅ COOH
C ₆ H ₅ COCl C ₆ H ₅ COOR	H ₂ O H ₂ O	



9.2 Chemical properties



10.0 ACID DERIVATIVES

Replacement of –OH group from a carboxylic group (–COOH) by a nucleophile like Cl^- , CH_3COO^- , $C_9H_5O^-$, NH_2^- , forms acid derivatives.

$$\begin{array}{c|c}
O & O \\
\parallel & \parallel \\
R-C-OH \xrightarrow{-OH} & R-C-Z \\
Acid & Acid derivative
\end{array}$$

O
$$\parallel$$
 R—C— is Acyl group and Z is nucleophile Cl^{Θ} , CH_3COO^{Θ} , $C_2H_5O^{\Theta}$, NH_2^{Θ}

Characteristic reaction for acid derivatives is nucleophilic substitution reaction:

Mechanism:

$$CH_{3}-C+Nu\longrightarrow CH_{3}-C-Nu+Z^{0}$$

$$Z$$

$$CH_{3}-C+Nu\longrightarrow CH_{3}-C-Nu+Z^{0}$$

In this reaction Z is leaving group. Weak bases are good leaving groups.

 $\textbf{Reactivilty order:} \quad \boxed{ \text{CH}_{3}\text{COCl} > \text{CH}_{3}\text{COOCOCH}_{3} > \text{CH}_{3}\text{COOC}_{2}\text{H}_{5} > \text{CH}_{3}\text{CONH}_{2} }$



10.1 Acetyl Chloride

Replacement of —OH group from a —COOH group by Cl— atom gives acid chloride.

$$\begin{array}{cccc} O & & O \\ \parallel & \parallel & \parallel \\ R-C-OH & \xrightarrow{-OH} & R-C-Cl \end{array}$$

10.1.1 General Method of Preparation:

(a) By heating CH₃COOH with PCl₃, PCl₅ & SOCl₂:

(i)
$$CH_3COOH + PCl_3 \longrightarrow CH_3COCl + H_3PO_3$$

(ii)
$$CH_3COOH + PCl_5$$
 \longrightarrow $CH_3COCl + POCl_3 + HCl_3$

(iii)
$$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2^{\uparrow} + HCl^{\uparrow}$$

(b) By heating the salt of acids with PCl₃, PCl₅ or SOCl₂:

(i)
$$CH_3COONa + PCl_3 \longrightarrow CH_3COCl + Na_3PO_3$$

(ii)
$$CH_3COONa + PCl_5$$
 \longrightarrow $CH_3COCl + POCl_3 + NaCl$

(iii)
$$CH_3COONa + SOCl_2 \longrightarrow CH_3COCl + SO_2 + NaCl$$

10.1.2 Physical properties:

- Pungent smelling liquid.
- (ii) Boiling point 52°C.
- (iii) Soluble in organic solvent, slowly soluble in water.

1° Amine

2° amine

Alcohol

(iv) It produces fumes in moist air due to the formation of HCl.

10.1.3 Chemical properties:

(a) Hydrolysis: CH₃CO Cl + H OH — CH₃COOH + HCl

(b) Reaction with active H - containing compounds (Acetylation) :

(i)
$$CH_3COCI + HNH_2 \longrightarrow CH_3CONH_2 + HCI$$

(ii)
$$CH_3COCI + HNH-R \longrightarrow CH_3CONHR + HCI$$

(iii)
$$CH_3COCI + HNR_2$$
 \longrightarrow $CH_3CONR_2 + HCI$

(iv)
$$CH_3CO[CI + H]OR$$
 \longrightarrow $CH_3COOR + HCI$

(Acetyl salicylic acid)

Aspirin

Alkyl acetate

+ HCl

N, N- dialkyl acetamide



(vi)
$$CH_3-C-CI+H-NH-NH_2-\cdots + CH_3-C-NHNH_2+HCI$$

Acetyl hydrazide

$$\begin{bmatrix} O \\ II \\ R-C-R + NH_2NH_2 \longrightarrow & R \\ Ketone & R \\ & hydrazone \end{bmatrix}$$

(vii)
$$OH + CH_3COCI \longrightarrow OCOCH_3 + HCI$$

(Phenyl acetate)

(c) Reduction:

(i)
$$CH_3COCl + H_2$$
 $\xrightarrow{Pd/BaSO_4}$ CH_3CHO (Rosenmund's reduction)

(ii)
$$CH_3COCl + 4H$$
 $\xrightarrow{(1)LiAlH_4}$ $CH_3CH_2OH + HCl$

(d) With Sodium acetate:
$$CH_3CO$$
 $Cl + Na$ $O - C - CH_3$ $Acetic anhydride$

(e) With Sodium ethoxide :
$$CH_3COC_1 + N_2OC_2H_5 \longrightarrow CH_3COOC_2H_5 + N_3COOC_2H_5 + N_3COOC_2H_$$

Ethyl acetate

(f) Friedel crafts reaction :
$$\bigcirc$$
 + CH₃COCl $\xrightarrow{AlCl_3}$ + HCl

Acetophenone

10.2 Acetic Anhydride (Ethanoic Anhydride)

10.2.1 General Method of Preparation:

(a) By heating acetyl Chloride with anhydrous sodium acetate [Lab. Method]:

(b) By Dehydration of acetic acid:

10.2.2 Physical Properties:

- (i) It is pungent smelling liquid.
- (ii) Sparingly soluble in water, soluble in ether & alcohol.
- (iii) Boiling point 139°C.



Pre-Medical

10.2.3 Chemical Properties:

(a) Hydrolysis :
$$CH_3CO - O + COCH_3 - CH_3COOH + CH_3COOH$$

Hydrolysis order: Alkaline > Acidic > neutral

$$N_a^{\dagger}$$
 OH
 $CH_3CO-O+COCH_3$ \longrightarrow CH_3COON_a + CH_3COOH

sodium acetate Acetic acid

(b) Reaction with active H - containing compounds (Acetylation) :

(i)
$$CH_3$$
— CO — $OCOCH_3 + H$ NH_2 \longrightarrow $CH_3CONH_2 + CH_3COOH$

(ii)
$$CH_3CO - OCOCH_3 + H NHR \longrightarrow CH_3CONHR + CH_3COOH$$

(iii)
$$CH_3CO - COCH_3 + H NR_2 \longrightarrow CH_3CONR_2 + CH_3COOH$$

(c) **Reduction**: With LiAlH₄ in ether gives ethyl alcohol

$$CH_3CO -O -COCH_3$$
 $\xrightarrow{LiAlH_4}$ $2CH_3CH_2OH + H_2O$

(d) Reaction with PCl₅ & SOCl₂:

$$CH_3CO + O + COCH_3 \longrightarrow 2CH_3COCI + POCI_3$$
 $CI + PCI_3 + CI$

Phosphorous Oxychloride

$$\begin{array}{ccc} \text{CH}_3\text{CO} & \text{O} & \text{COCH}_3 & \longrightarrow & 2\text{CH}_3\text{COCl} + \text{SO}_2 \\ \text{Cl} & \text{SO} & \text{Cl} & \end{array}$$

10.2.4 Uses

- (i) As an acetylating agent
- (ii) In the manufacture of cellulose acetate, aspirin, phenacetin, acetamide, & acetophenone etc.
- (iii) For detection and estimation of hydroxyl and amino group.

10.3 Ethyl acetate

10.3.1 General Method of Preparation:

(a) **Tischenko reaction**: By treating acetaldehyde with aluminium ethoxide. (Modified cannizaro reaction)

2CH₃CHO
$$\xrightarrow{(C_2H_5O)_3Al}$$
 CH₃COOC₂H₅
Ethyl acetate

(b) Esterification :
$$CH_3$$
— C — OH + HO — C_2H_5 $\xrightarrow{Conc.H_2SO_4}$ CH_3 — C — OC_2H_5 + H_2O Ethylacetate

BEGINNER'S BOX-6

- 1. Alkanoic acids can be prepared by hydrolysis of:-
 - (1) Trihaloalkanes

(2) 1,1,1-trihaloalkanes

(3) Grignard reagents

- (4) Ketones
- 2. Acids have much higher boiling points than isomeric esters because :-
 - (1) Acids form dimers by H–Bonding
 - (2) Acids are volatile in steam
 - (3) Esters are non-volatile
 - (4) Acids can ionise to give protons in aqueous solution
- 3. Which of the following compounds can form intermolecular H-bonds:-
 - (1) Ethyl acetate

(2) Methyl formate

(3) Acetamide

- (4) Acetic anhydride
- 4. Reaction of ethyl acetate with sodium ethoxide gives acetoacetic ester. This reaction is known with the name of :-
 - (1) Claisen

(2) Clemmensen

(3) Cannizaro

(4) Etard

10.3.2 Physical Properties

- (i) Fruity smell liquid.
- (ii) Boling point 77° C.
- (iii) Slightly soluble in water, soluble in organic solvent.

10.3.3 Chemical Properties:

(a) Hydrolysis: In acidic medium reaction is reversible and in alkaline medium reaction is irreversible.

$$H^+$$
 CH₃COOH + C₂H₅OH

$$CH_3COOC_2H_5 + NaOH \longrightarrow$$

$$\rightarrow$$
 CH₃COONa + C₂H₅OH

- **(b) Ammonolysis**: $CH_3COOC_2H_5 + HNH_2 \xrightarrow{\Delta} CH_3CONH_2 + C_2H_5OH$
 - Acetamide Ethanol
- (c) Reaction with NH₂NH₂ & NH₂OH:

$$CH_3COOC_2H_5 + HNHNH_2 \xrightarrow{\Delta} CH_3CONHNH_2 + C_2H_5OH$$

Hydrazine Acetyl hydrazide

$$CH_{3}CO \boxed{OC_{2}H_{5} + H} NHOH \stackrel{\Delta}{\longrightarrow} CH_{3}CONHOH + C_{2}H_{5}OH$$

hydroxyl amine Acetyl hydroxamic acid

- (d) Reduction : $CH_3COOC_2H_5 \xrightarrow{LiAlH_4} CH_3CH_9OH + C_9H_6OH$
- (e) Claisen condensation:



10.4 Acetamide

10.4.1 General Method of Preparation:

(a) Ammonolysis of acid derivatives :

$$CH_{3}CO\boxed{Cl+H}NH_{2} \longrightarrow CH_{3}CONH_{2} + HCl$$

$$CH_{3}CO\boxed{-O-COCH_{3}+H}NH_{2} \longrightarrow CH_{3}CONH_{2} + CH_{3}COOH$$

$$CH_{3}CO\boxed{OC_{2}H_{5}+H}NH_{2} \stackrel{\Delta}{\longrightarrow} CH_{3}CONH_{2} + C_{2}H_{5}OH$$

(b) Hydrolysis of alkyl cyanides : By the partial hydrolysis of alkyl cyanides.

$$R - C \equiv N + H_2O \longrightarrow R - C - NH_2$$

$$0$$

$$CH_3 - C \equiv N + H_2O \longrightarrow CH_3 - C - NH_2$$

$$0$$

10.4.2 Physical Properties:

- (i) Acetamide is white crystalline solid.
- (ii) Pure acetamide is odourless.
- (iii) Impure acetamide Smell like mouse.
- (iv) Lower amides are soluble in water, due to H-bonding.
- (v) Their higher M. P. and B. P. are due to intermolecular H-bonding.

10.4.3 Chemical Properties:

(a) Hydrolysis : Amides are hydrolysed rapidly in acidic medium. In alkaline medium hydrolysis is carried out in temperature condition.

$$R - C - NH_2 + H_2O \xrightarrow{H^+} R - COOH + \stackrel{\dagger}{N}H_4$$

$$CH_3 - C - NH_2 + NaOH \xrightarrow{\Delta} CH_3COONa + NH_3 \uparrow$$

(b) Reduction to primary amines : Amine contains same number of carbon atoms.

$$CH_{3}CONH_{2} \qquad \xrightarrow{LiAlH_{4} \text{ or} \atop Na/C_{2}H_{5}OH} \qquad CH_{3}CH_{2}NH_{2} + H_{2}O$$

1° amine

(c) Dehydration with PCl₅, SOCl₂ or P₂O₅:



(d) Reaction with nitrous acid:

$$\begin{array}{c|c} CH_3-CO+N & H_2 & \xrightarrow{\quad HNO_2 \quad} CH_3COOH + N_2 + H_2O \\ & HO-N \neq O \end{array}$$

(e) Hoffmann's bromamide degradation reaction : Amides on reaction with bromine, and NaOH or KOH yield primary amines, having one C-atom less than the amides.

$$CH_3CONH_2 + Br_2 + KOH(aq.)$$
 \longrightarrow $CH_3NH_2 + KBr + K_2CO_3 + H_2O$ or (KOBr)

Mechanism:

ANSWER'S KEY

Que.	1	2	3							
Ans.	3	4	2							
Que.	1	2								
Ans.	1	2								
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Que.	1	2	3							
Ans.	3	2	3							
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Que.	1	2	3							
Ans.	2	4	1							
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Que.	1	2	3							
Ans.	4	2	3							
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