Table of Contents

1. Aldehydes and Ketones
2. Oxidation of Alcohols
3. Catalytic Dehydrogenation
4. Reductive Ozonolysis
5. Rosenmund Reduction
6. Reduction of Nitriles
7. Esters Reduction
8. Acyl Chlorides and Organometallics
9. Gatterman-Koch Reaction
10. Friedel-Crafts Acylation
11. Alkynes to Aldehydes and Ketones
12. Oxidation of 1,2-Glycols
13. Etard Reaction
14. Side Chain Chlorination
15. Physical Properties
16. Polarity of Carbonyl Group
17. Acidity of α-Hydrogen
18. Nucleophilic Addition Reactions
19. Nucleophilic Addition-Elimination Reactions
20. Oxidation and Reduction Reactions
21. Haloform Reaction
22. Aldol Condensation
23. Cannizzaro Reaction
24. Distinction Between Aldehydes and Ketones
25. Uses of Aldehydes and Ketones
26. Methods of Preparation of Carboxylic Acids
27. Physical Properties
28. Reactions Involving Cleavage of O — H Bond
29. Reactions Involving Cleavage of C—OH Bond
30. Reactions Involving COOH Group
31. Uses of Carboxylic Acids

Aldehydes and Ketones

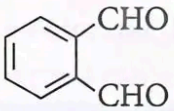
Introduction

- Aldehydes and ketones contain a carbonyl group (>C=O) with general formula $C_nH_{2n}O$.
- Aldehydes have the carbonyl group attached to at least one hydrogen atom.
- Ketones have the carbonyl group attached to two carbon atoms (alkyl or aryl groups).
- Carboxylic acids contain the —COOH group with general formula $C_nH_{2n}O_2$.

Nomenclature

- Common aldehyde names come from corresponding carboxylic acids by replacing '-ic acid' with 'aldehyde'.
- Substituent positions are indicated by Greek letters α, β, γ, δ starting from the carbon next to the carbonyl group.
- Common ketone names are derived from the two alkyl or aryl groups attached to the carbonyl carbon.
- IUPAC names for aldehydes replace the alkane '-e' ending with '-al'.
- IUPAC names for ketones replace the alkane '-e' ending with '-one'.

Common and IUPAC names of some aldehydes and ketones

Structure	Common name	IUPAC name
Aldehyde		
$HCHO$	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
$(CH_3)_2CHCHO$	Isobutyraldehyde	2-Methylpropanal
$CH_3CH(OCH_3)CHO$	α-Methoxypropionaldehyde	2-Methoxypropanal
$CH_3CH_2CH_2CH_2CHO$	Valeraldehyde	Pentanal
$CH_2=CHCHO$	Acrolein	Prop-2-enal
	Phthaldehyde	Benzene-1,2-dicarbaldehyde
Ketone		
$CH_3COCH_2CH_2CH_3$	Methyl *n*-propyl ketone	Pentan-2-one
$(CH_3)_2CHCOCH(CH_3)_2$	Di-isopropyl ketone	2,4-Dimethylpentan-3-one
$(CH_3)_2C=CHCOCH_3$	Mesityl oxide	4-Methylpent-3-en-2-one

Structure

- Carbonyl carbon is sp^2 hybridized, forming three sigma bonds and one pi bond with oxygen.
- The carbonyl carbon and attached atoms lie in the same plane with bond angles of 120° (trigonal planar).
- Pi electron cloud is above and below the plane of the carbonyl group.
- Carbonyl compounds exhibit resonance: $C=O \leftrightarrow C^{+}–O^{-}$.

Solved Examples

- **Ex 1:** Name CH_3CHO using IUPAC and common names.
  Step 1: Identify aldehyde group.
  Step 2: Common name: Acetaldehyde.
  Step 3: IUPAC name: Ethanal.
- **Ex 2:** Identify the hybridization of carbonyl carbon in acetone.
  Step 1: Carbonyl carbon forms three sigma bonds and one pi bond.
  Step 2: Hybridization is sp^2.

Practice Set

- Q1: Which of the following is an aldehyde?
  A. Propanone
  B. Propanal
  C. Benzophenone
  D. Acetophenone
- Q2: The IUPAC name of CH_3COCH_3 is:
  A. Propanal
  B. Propanone
  C. Propanol
  D. Propanoic acid
- Q3: Which statement about carbonyl compounds is correct?
  A. Carbonyl carbon is sp^3 hybridized.
  B. Carbonyl group has bond angle 109.5°.
  C. Carbonyl compounds show resonance.
  D. Carbonyl carbon forms four sigma bonds.

Answer Key

- Q1: B - Propanal is an aldehyde with carbonyl group attached to one H and one alkyl group.
- Q2: B - Propanone is the IUPAC name for CH_3COCH_3, a ketone.
- Q3: C - Carbonyl compounds show resonance between C=O and $C^+–O^-$ forms.

Memory Aids

- Aldehyde names end with '-al', ketones with '-one'.
- Greek letters α, β, γ indicate substituent positions next to carbonyl.
- Carbonyl carbon is always sp^2 hybridized with trigonal planar geometry.
- Resonance stabilizes carbonyl compounds: C=O ↔ $C^+–O^-$.

Oxidation of Alcohols

Explanation

- Primary alcohols oxidize to aldehydes; further oxidation gives carboxylic acids.
- Secondary alcohols oxidize to ketones.
- Oxidizing agents: potassium dichromate ($K_2Cr_2O_7$) in acidic medium.
- Reaction example: $RCH_2OH + [O] \rightarrow RCHO$ (aldehyde)
- Secondary alcohol: $R_2CHOH + [O] \rightarrow R_2C=O$ (ketone)

Solved Examples

- Ex 1: Oxidize ethanol with $K_2Cr_2O_7/H_2SO_4$ → forms ethanal (acetaldehyde).
- Ex 2: Oxidize isopropanol → forms acetone (a ketone).

Practice Set

- Q1: Which product forms when primary alcohol is oxidized partially?
  - A. Carboxylic acid
  - B. Aldehyde
  - C. Ketone
  - D. Alkane
- Q2: Which reagent is commonly used for oxidation of alcohols?
  - A. $LiAlH_4$
  - B. $K_2Cr_2O_7/H_2SO_4$
  - C. $NaBH_4$
  - D. Zn/HCl
- Q3: Secondary alcohol oxidation yields?
  - A. Aldehyde
  - B. Ketone
  - C. Carboxylic acid
  - D. Alkene

Answer Key

- Q1: B - Partial oxidation of primary alcohols forms aldehydes.
- Q2: B - $K_2Cr_2O_7/H_2SO_4$ is a strong oxidizing agent.
- Q3: B - Secondary alcohols oxidize to ketones only.

Memory Aids

- Primary alcohol → Aldehyde → Acid (if over-oxidized)
- Secondary alcohol → Ketone only
- $K_2Cr_2O_7$ is a common oxidizer

Catalytic Dehydrogenation

Explanation

- Alcohols heated with copper catalyst lose hydrogen gas (H_2).
- Primary alcohols form aldehydes; secondary alcohols form ketones.
- No over-oxidation occurs as in chemical oxidants.
- Reaction: $RCH_2OH \rightarrow RCHO + H_2$ (catalyst: Cu, heat)

Solved Examples

- Ex 1: Ethanol heated with Cu → ethanal + H_2.
- Ex 2: Isopropanol heated with Cu → acetone + H_2.

Practice Set

- Q1: Catalyst used in catalytic dehydrogenation?
  - A. Pd
  - B. Cu
  - C. Fe
  - D. Ni
- Q2: Product of catalytic dehydrogenation of secondary alcohol?
  - A. Aldehyde
  - B. Ketone
  - C. Alcohol
  - D. Alkane
- Q3: Which gas is released during catalytic dehydrogenation?
  - A. O_2
  - B. CO_2
  - C. H_2
  - D. N_2

Answer Key

- Q1: B - Copper is the catalyst used.
- Q2: B - Secondary alcohols form ketones.
- Q3: C - Hydrogen gas is released.

Memory Aids

- Cu catalyst + heat → dehydrogenation
- Primary alcohol → aldehyde + H_2
- Secondary alcohol → ketone + H_2

Reductive Ozonolysis

Explanation

- Alkenes react with ozone (O_3) to cleave double bonds.
- In reductive workup (Zn/H_2O), aldehydes are formed.
- Reaction: RCH=CHR' + O_3 → RCHO + R'CHO (aldehydes)

Solved Examples

- Ex 1: Ozonolysis of ethene → 2 molecules of formaldehyde.
- Ex 2: Ozonolysis of propene → acetaldehyde + formaldehyde.

Practice Set

- Q1: Ozone cleaves which bond in alkenes?
  - A. C–H
  - B. C=C double bond
  - C. C–C single bond
  - D. C–O bond
- Q2: Reductive ozonolysis uses which reagent for workup?

    - A. H_2O_2
    - B. Zn/H_2O
    - C. $KMnO_4$
    - D. $NaBH_4$
- Q3: Products of reductive ozonolysis of alkene?
    - A. Ketones only
    - B. Aldehydes only
    - C. Alcohols
    - D. Carboxylic acids

Answer Key

- Q1: B - Ozone cleaves C=C double bonds.
- Q2: B - Zn/H_2O is used for reductive workup.
- Q3: B - Aldehydes are formed in reductive ozonolysis.

Memory Aids

- O_3 breaks double bonds → aldehydes (with Zn/H_2O)
- Reductive workup prevents acid formation

Rosenmund Reduction

Explanation

- Acyl chlorides (RCOCl) are reduced to aldehydes using H_2 and Pd on $BaSO_4$ catalyst.
- Reaction: RCOCl + H_2 → RCHO + HCl (catalyst: $Pd/BaSO_4$)
- Selective reduction stops at aldehyde stage.

Solved Examples

- Ex 1: Benzoyl chloride + $H_2/Pd\text{-}BaSO_4$ → benzaldehyde.

Practice Set

- Q1: Catalyst used in Rosenmund reduction?
  - A. Pd on $BaSO_4$
  - B. Pt
  - C. Ni
  - D. Cu
- Q2: Product of Rosenmund reduction of acyl chloride?
  - A. Alcohol
  - B. Aldehyde
  - C. Ketone
  - D. Carboxylic acid
- Q3: Which gas is used in Rosenmund reduction?
  - A. O_2
  - B. H_2
  - C. N_2
  - D. CO

Answer Key

- Q1: A - Pd on $BaSO_4$ is the catalyst.
- Q2: B - Acyl chlorides reduce to aldehydes.
- Q3: B - Hydrogen gas is used.

Memory Aids

- Rosenmund: Acyl chloride + H_2 + $Pd/BaSO_4$ → Aldehyde
- $BaSO_4$ reduces catalyst activity to stop at aldehyde

Reduction of Nitriles

Explanation

- Nitriles (R–CN) reduce to aldehydes by controlled partial reduction.
- Reagents: DIBAL-H at low temperature or other selective reducing agents.
- Reaction: R–CN + 1 eq. DIBAL-H → R–CHO (aldehyde)

Solved Examples

- Ex 1: Benzonitrile + DIBAL-H (–78°C) → benzaldehyde.

Practice Set

- Q1: Nitriles reduce to?
  - A. Alcohols
  - B. Aldehydes
  - C. Ketones
  - D. Carboxylic acids
- Q2: Common reagent for partial nitrile reduction?
  - A. $LiAlH_4$
  - B. DIBAL-H
  - C. $NaBH_4$
  - D. H_2/Pd
- Q3: Temperature condition for nitrile reduction to aldehyde?
  - A. Room temperature
  - B. High temperature
  - C. Low temperature (–78°C)
  - D. 100°C

Answer Key

- Q1: B - Nitriles reduce to aldehydes selectively.
- Q2: B - DIBAL-H is used for partial reduction.

- Q3: C - Low temperature prevents over-reduction.

Memory Aids

- DIBAL-H at −78°C stops reduction at aldehyde stage
- Nitrile → Aldehyde (partial reduction)

Esters Reduction

Explanation

- Esters reduce to aldehydes using DIBAL-H at low temperature.
- After hydrolysis (adding water), aldehydes are obtained.
- Reaction: RCOOR' + DIBAL-H → RCHO (after H_2O workup)

Solved Examples

- Ex 1: Ethyl acetate + DIBAL-H (−78°C) + H_2O → acetaldehyde.

Practice Set

- Q1: Reagent for ester to aldehyde conversion?
  - A. $LiAlH_4$
  - B. DIBAL-H
  - C. $NaBH_4$
  - D. H_2/Pd
- Q2: Temperature condition for ester reduction?
  - A. Room temperature
  - B. High temperature
  - C. Low temperature (−78°C)
  - D. 100°C
- Q3: Product after ester reduction and hydrolysis?
  - A. Alcohol

- B. Aldehyde
- C. Ketone
- D. Acid

Answer Key

- Q1: B - DIBAL-H is selective for aldehyde formation.
- Q2: C - Low temperature prevents full reduction.
- Q3: B - Aldehydes form after hydrolysis.

Memory Aids

- DIBAL-H + low temp → ester to aldehyde
- Hydrolysis step is essential after reduction

Acyl Chlorides and Organometallics

Explanation

- Acyl chlorides react with organomagnesium (Grignard) or organocadmium reagents.
- Reaction with Grignard gives tertiary alcohols (overreaction).
- Reaction with organocadmium reagents gives ketones selectively.
- Reaction: RCOCl + R'MgX → RCOR' (ketone) with organocadmium reagent.

Solved Examples

- Ex 1: Benzoyl chloride + $R_2CuMgBr$ → benzophenone (ketone).

Practice Set

- Q1: Product of acyl chloride + organocadmium reagent?
  - A. Aldehyde

    - B. Ketone
    - C. Alcohol
    - D. Acid
- Q2: Reaction of acyl chloride with Grignard reagent yields?
    - A. Ketone
    - B. Aldehyde
    - C. Tertiary alcohol
    - D. Carboxylic acid
- Q3: Organocadmium reagents are preferred because?
    - A. They give aldehydes
    - B. They stop at ketone stage
    - C. They reduce to alcohols
    - D. They form acids

Answer Key

- Q1: B - Organocadmium reagents give ketones.
- Q2: C - Grignard reagents overreact to tertiary alcohols.
- Q3: B - Organocadmium stops at ketone stage.

Memory Aids

- Acyl chloride + organocadmium → ketone
- Acyl chloride + Grignard → tertiary alcohol

Gatterman-Koch Reaction

Explanation

- Benzene reacts with CO and HCl in presence of $AlCl_3$ and CuCl catalysts.
- Forms benzaldehyde by electrophilic substitution.
- Reaction: $C_6H_6 + CO + HCl \rightarrow C_6H_5CHO$

Solved Examples

- Ex 1: Benzene + CO + HCl + $AlCl_3$/CuCl → benzaldehyde.

Practice Set

- Q1: Gatterman-Koch reaction requires which gas?
  - A. CO
  - B. CO_2
  - C. H_2
  - D. O_2
- Q2: Product of Gatterman-Koch reaction?
  - A. Acetophenone
  - B. Benzaldehyde
  - C. Phenol
  - D. Benzoic acid
- Q3: Catalysts used in Gatterman-Koch?
  - A. $AlCl_3$ and CuCl
  - B. $FeCl_3$
  - C. Pd/C
  - D. $ZnCl_2$

Answer Key

- Q1: A - Carbon monoxide is required.
- Q2: B - Benzaldehyde is the product.
- Q3: A - $AlCl_3$ and CuCl are catalysts.

Memory Aids

- Gatterman-Koch: Benzene + CO + HCl + $AlCl_3$/CuCl → Benzaldehyde

Friedel-Crafts Acylation

Explanation

- Benzene reacts with acyl chlorides in presence of $AlCl_3$ catalyst.
- Forms aromatic ketones (acetophenone, benzophenone, etc.).
- Reaction: C_6H_6 + RCOCl → C_6H_5COR (ketone)

Solved Examples

- Ex 1: Benzene + acetyl chloride + $AlCl_3$ → acetophenone.

Practice Set

- Q1: Catalyst in Friedel-Crafts acylation?
  - A. $AlCl_3$
  - B. $FeCl_3$
  - C. Cu
  - D. Pd
- Q2: Product of Friedel-Crafts acylation?
  - A. Aldehyde
  - B. Ketone
  - C. Alcohol
  - D. Acid
- Q3: Friedel-Crafts acylation is an example of?
  - A. Electrophilic substitution
  - B. Nucleophilic substitution
  - C. Addition reaction
  - D. Elimination reaction

Answer Key

- Q1: A - $AlCl_3$ is the catalyst.
- Q2: B - Aromatic ketones are formed.

- Q3: A - It is electrophilic substitution.

Memory Aids

- Friedel-Crafts: Acyl chloride + $AlCl_3$ → Aromatic ketone

Alkynes to Aldehydes and Ketones

Explanation

- Alkynes undergo hydration or hydroboration-oxidation to form aldehydes or ketones.
- Terminal alkynes give aldehydes; internal alkynes give ketones.
- Hydration: R–C≡CH + H_2O ($HgSO_4$, H_2SO_4) → ketone.
- Hydroboration-oxidation: R–C≡CH + 1) R_2BH 2) H_2O_2/OH^- → aldehyde.

Solved Examples

- Ex 1: Hydration of 1-butyne → methyl ketone.
- Ex 2: Hydroboration-oxidation of 1-butyne → aldehyde.

Practice Set

- Q1: Product of terminal alkyne hydroboration-oxidation?
  - A. Ketone
  - B. Aldehyde
  - C. Alcohol
  - D. Acid
- Q2: Catalyst for alkyne hydration?
  - A. $HgSO_4$, H_2SO_4
  - B. $AlCl_3$
  - C. Pd/C
  - D. Cu
- Q3: Internal alkyne hydration yields?

    - A. Aldehyde
    - B. Ketone
    - C. Alcohol
    - D. Alkene

Answer Key

- Q1: B - Terminal alkynes give aldehydes by hydroboration-oxidation.
- Q2: A - $HgSO_4$ and H_2SO_4 catalyze hydration.
- Q3: B - Internal alkynes give ketones.

Memory Aids

- Terminal alkyne + hydroboration-oxidation → aldehyde
- Internal alkyne + hydration → ketone

Oxidation of 1,2-Glycols

Explanation

- Vicinal diols (1,2-glycols) cleave upon oxidation with lead tetraacetate.
- Cleavage forms aldehydes or ketones depending on substituents.
- Reaction: R–CHOH–CHOH–R' + $Pb(OAc)_4$ → RCHO + R'CHO or ketones

Solved Examples

- Ex 1: Ethylene glycol + $Pb(OAc)_4$ → 2 formaldehyde molecules.

Practice Set

- Q1: Oxidizing agent for 1,2-glycols?
    - A. $KMnO_4$

    - B. $Pb(OAc)_4$
    - C. $K_2Cr_2O_7$
    - D. O_3
- Q2: Products of 1,2-glycol oxidation?
    - A. Alcohols
    - B. Aldehydes or ketones
    - C. Acids
    - D. Alkenes
- Q3: 1,2-glycol oxidation cleaves?
    - A. C–C bond between hydroxyl groups
    - B. C–H bond
    - C. C–O bond
    - D. C=C bond

Answer Key

- Q1: B - Lead tetraacetate is used.
- Q2: B - Aldehydes or ketones form.
- Q3: A - Cleaves C–C bond between OH groups.

Memory Aids

- $Pb(OAc)_4$ cleaves vicinal diols to aldehydes/ketones

Etard Reaction

Explanation

- Methylbenzenes oxidize to benzaldehydes using chromium reagents (Etard reagent).
- Reaction: $C_6H_5CH_3 + CrO_3 \rightarrow C_6H_5CHO$

Solved Examples

- Ex 1: Toluene + Etard reagent → benzaldehyde.

Practice Set

- Q1: Etard reagent contains?
  - A. Chromium
  - B. Manganese
  - C. Copper
  - D. Iron
- Q2: Product of Etard reaction?
  - A. Benzyl alcohol
  - B. Benzaldehyde
  - C. Benzoic acid
  - D. Toluene
- Q3: Etard reaction oxidizes?
  - A. Benzene ring
  - B. Methyl side chain
  - C. Carboxyl group
  - D. Hydroxyl group

Answer Key

- Q1: A - Chromium is the key element.
- Q2: B - Benzaldehyde is formed.
- Q3: B - Methyl side chain is oxidized.

Memory Aids

- Etard: Methylbenzene + Cr reagent → Benzaldehyde

Side Chain Chlorination

Explanation

- Methyl groups on benzene rings are chlorinated using Cl_2 and light.
- Chloromethyl group hydrolyzes to benzaldehyde.
- Reaction: $C_6H_5CH_3 + Cl_2 \rightarrow C_6H_5CH_2Cl \rightarrow C_6H_5CHO$ (after hydrolysis)

Solved Examples

- Ex 1: Toluene + Cl_2/hv → benzyl chloride → benzaldehyde.

Practice Set

- Q1: Reagent for side chain chlorination?
  - A. Cl_2/hv
  - B. Br_2/hv
  - C. HCl
  - D. $KMnO_4$
- Q2: Product after hydrolysis of chloromethylbenzene?
  - A. Benzyl alcohol
  - B. Benzaldehyde
  - C. Benzoic acid
  - D. Toluene
- Q3: Side chain chlorination occurs at?
  - A. Benzene ring
  - B. Methyl side chain
  - C. Carboxyl group
  - D. Hydroxyl group

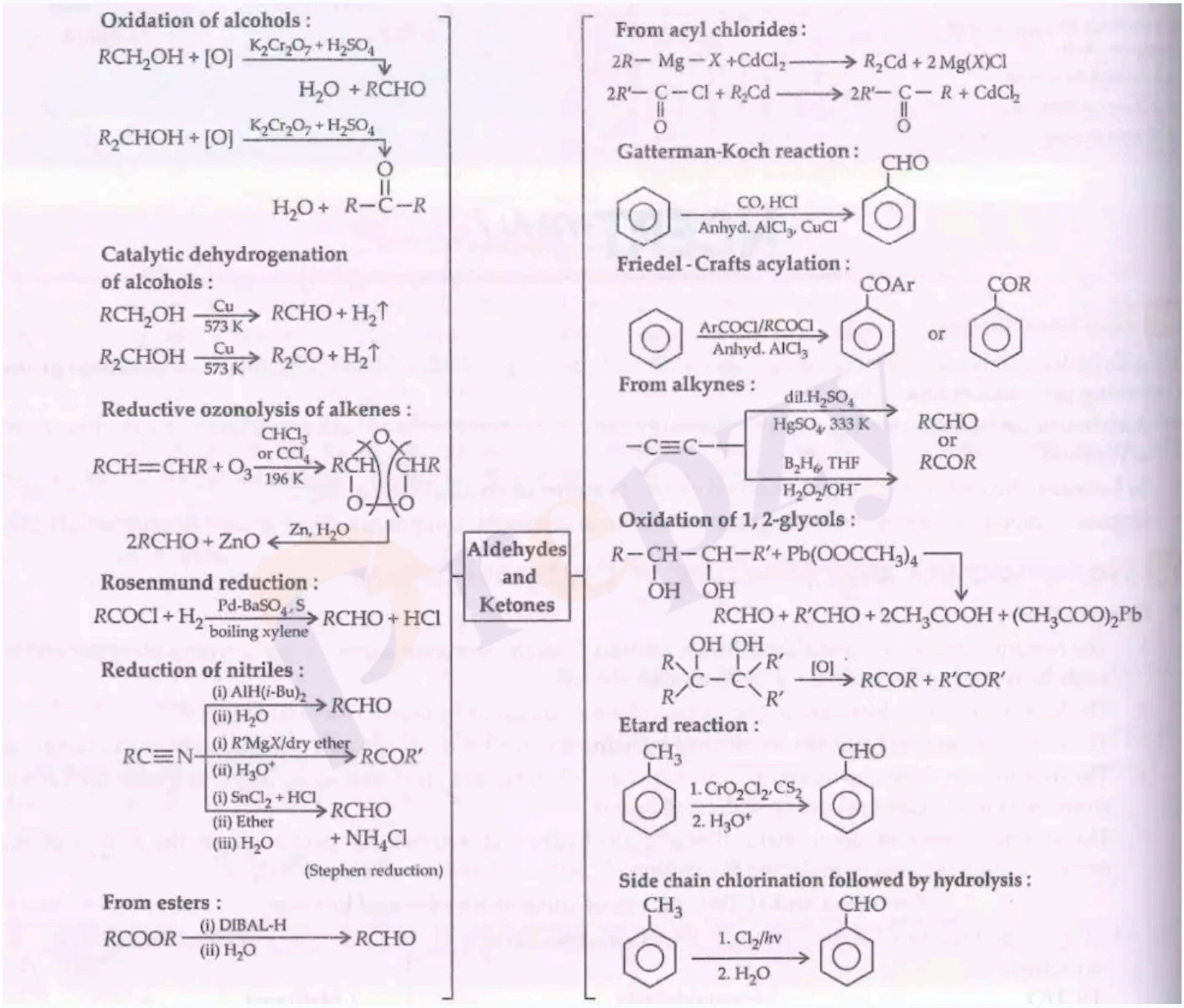
Answer Key

- Q1: A - Chlorine and light initiate chlorination.
- Q2: B - Benzaldehyde forms after hydrolysis.

- Q3: B - Methyl side chain is chlorinated.

Memory Aids

- Side chain chlorination: Cl_2/hv → benzyl chloride → benzaldehyde



Physical Properties

Physical State

- Lower aldehydes and ketones (up to C_{10}) are colourless, volatile liquids.
- Formaldehyde is a gas at room temperature.

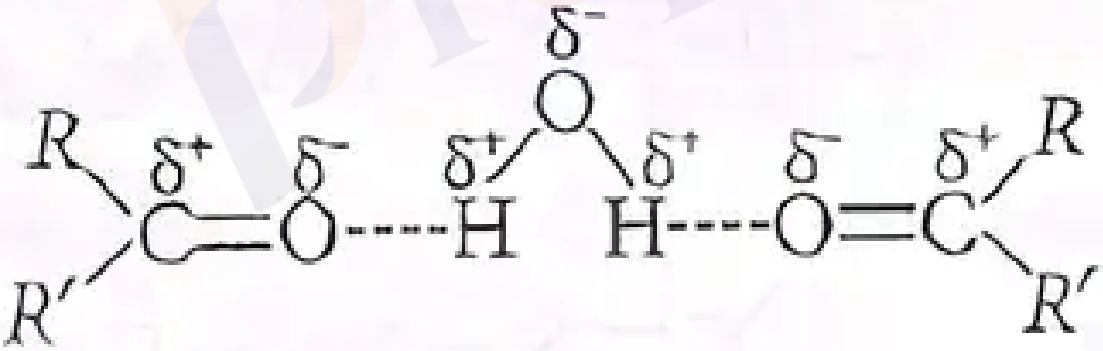
- Higher aldehydes and ketones are solids with fruity odour.
- Lower aldehydes have unpleasant odour; ketones have pleasant smell.

Boiling Points

- Boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of similar molecular mass due to dipole-dipole interactions.
- Boiling points are lower than alcohols of similar molecular mass due to absence of intermolecular hydrogen bonding.
- Ketones have slightly higher boiling points than isomeric aldehydes because two alkyl groups increase polarity of carbonyl group.

Solubility

- Lower aldehydes and ketones (up to C_4) are soluble in water due to hydrogen bonding between carbonyl group and water.
- Solubility decreases with increasing molecular weight.



Solved Examples

- **Ex 1:** Identify physical state of butanal (C_4H_8O) at room temperature.
  Answer: Butanal is a lower aldehyde (C_4), so it is a colourless, volatile liquid.
- **Ex 2:** Compare boiling points of propanal and acetone.
  Answer: Acetone (ketone) has slightly higher boiling point than propanal (aldehyde) due to two alkyl groups increasing polarity.

Practice Set

- **Q1:** Which of the following is a gas at room temperature?
  A. Acetaldehyde
  B. Formaldehyde
  C. Butanone
  D. Benzaldehyde
- **Q2:** Why do ketones have higher boiling points than isomeric aldehydes?
  A. Presence of hydrogen bonding
  B. Two electron releasing alkyl groups increase polarity
  C. Larger molecular mass
  D. Lower dipole moment
- **Q3:** Which compound is most soluble in water?
  A. Hexanal
  B. Propanone
  C. Octanal
  D. Nonanal

Answer Key

- **Q1:** B. Formaldehyde is a gas at room temperature, others are liquids or solids.
- **Q2:** B. Two alkyl groups in ketones increase polarity, raising boiling point.
- **Q3:** B. Propanone (a ketone with low molecular weight) is most soluble due to hydrogen bonding.

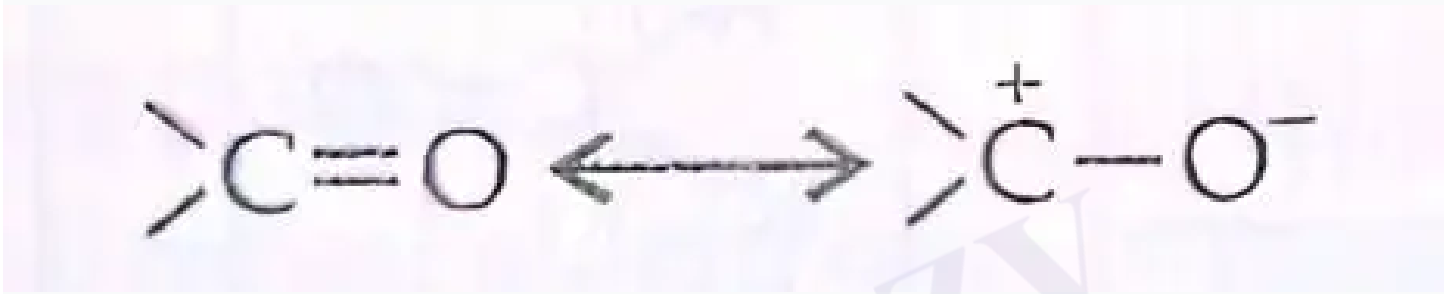
Memory Aids

- Formaldehyde = gas; others up to C_{10} = liquids.
- Ketones boil higher than aldehydes due to alkyl groups.
- Solubility decreases as chain length increases.

Polarity of Carbonyl Group

Explanation

- Carbonyl group (>C=O) is polar due to high electronegativity of oxygen.
- Carbonyl carbon is electrophilic (Lewis acid), oxygen is nucleophilic (Lewis base).
- Resonance structures show partial positive charge on carbon and negative on oxygen.
- High dipole moment (2.3-2.8 D) explained by resonance, not just inductive effect.
- Aldehydes and ketones undergo nucleophilic addition, unlike alkenes which undergo electrophilic addition.



Solved Examples

- Ex 1: Identify electrophilic and nucleophilic sites in carbonyl group.
  - Carbon is electrophilic due to partial positive charge.
  - Oxygen is nucleophilic due to partial negative charge.

Practice Set

- Q1: What is the nature of carbonyl carbon?
  - A. Nucleophilic
  - B. Electrophilic
  - C. Neutral
  - D. Radical
- Q2: Which explains the high dipole moment of carbonyl group?
  - A. Inductive effect only
  - B. Resonance structures
  - C. Hydrogen bonding
  - D. Van der Waals forces
- Q3: Aldehydes and ketones mainly undergo which type of reaction?

- A. Electrophilic addition
- B. Nucleophilic addition
- C. Free radical substitution
- D. Elimination

Answer Key

- Q1: B - Carbonyl carbon is electrophilic due to partial positive charge.
- Q2: B - Resonance structures explain the high dipole moment.
- Q3: B - Aldehydes and ketones undergo nucleophilic addition reactions.

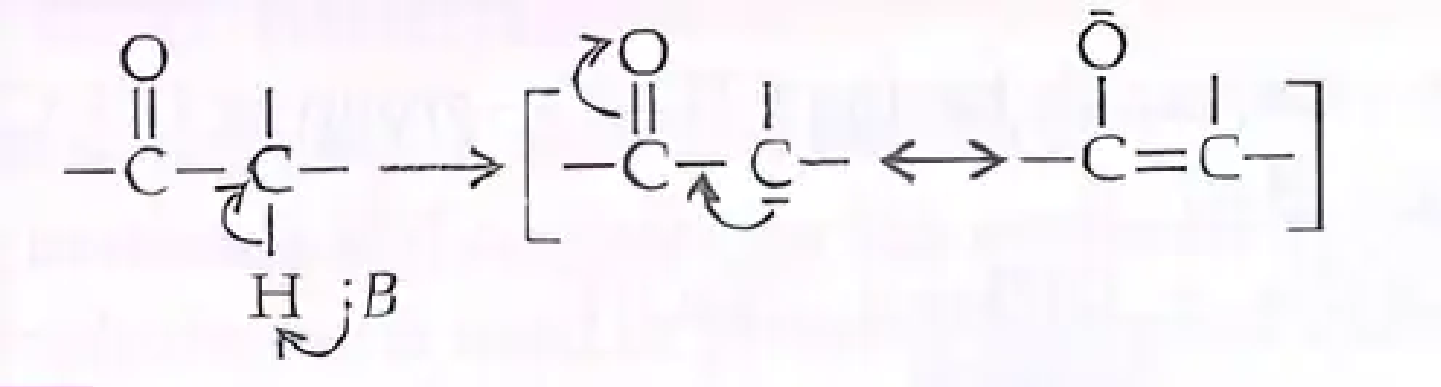
Memory Aids

- Carbonyl carbon = Electrophile (positive center).
- Oxygen = Nucleophile (negative center).
- Resonance increases polarity and reactivity.

Acidity of α-Hydrogen

Explanation

- α-Hydrogens in carbonyl compounds are acidic due to electron-withdrawing carbonyl group.
- Conjugate base (enolate ion) is resonance stabilized.
- Base removes α-hydrogen forming resonance-stabilized enolate ion.



Solved Examples

- Ex 1: Show formation of enolate ion from a carbonyl compound.
  - Base abstracts α-hydrogen.
  - Electrons shift to form double bond between carbons.
  - Electrons from C=O shift to oxygen, giving negative charge.

Practice Set

- Q1: Why are α-hydrogens acidic in carbonyl compounds?
  - A. Due to resonance stabilization of conjugate base
  - B. Due to inductive effect only
  - C. Due to steric hindrance
  - D. Due to hydrogen bonding
- Q2: What species is formed after removal of α-hydrogen?
  - A. Carbocation
  - B. Enolate ion
  - C. Free radical
  - D. Carbene
- Q3: Which effect stabilizes the enolate ion?
  - A. Inductive effect
  - B. Resonance
  - C. Hyperconjugation
  - D. Hydrogen bonding

Answer Key

- Q1: A - Resonance stabilization of conjugate base increases acidity.
- Q2: B - Enolate ion is formed after α-hydrogen removal.
- Q3: B - Resonance stabilizes the enolate ion.

Memory Aids

- α-Hydrogen acidity due to resonance stabilized enolate.
- Base removes α-H to form resonance structures.

Nucleophilic Addition Reactions

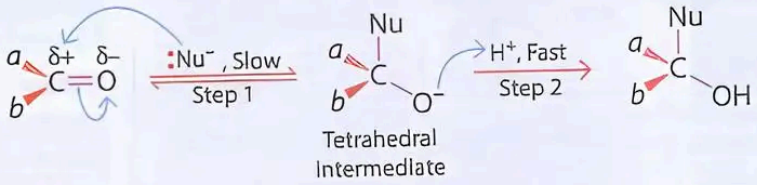
Explanation

- Nucleophile attacks electrophilic carbonyl carbon forming tetrahedral intermediate.
- Intermediate protonated to form alcohol or related product.
- Common nucleophiles: Grignard reagent, hydride ions, cyanide ion, hydroxide, alkoxides.
- Aldehydes are more reactive than ketones due to steric and electronic factors.
- Reactions include formation of cyanohydrins, bisulphite addition compounds, hemiacetals, acetals, and ketals.

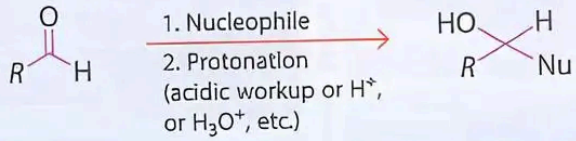
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Nucleophilic Addition Reaction

Two-Step Mechanism :



General Chemical Reactions of Aldehydes & Ketones



Bonds formed

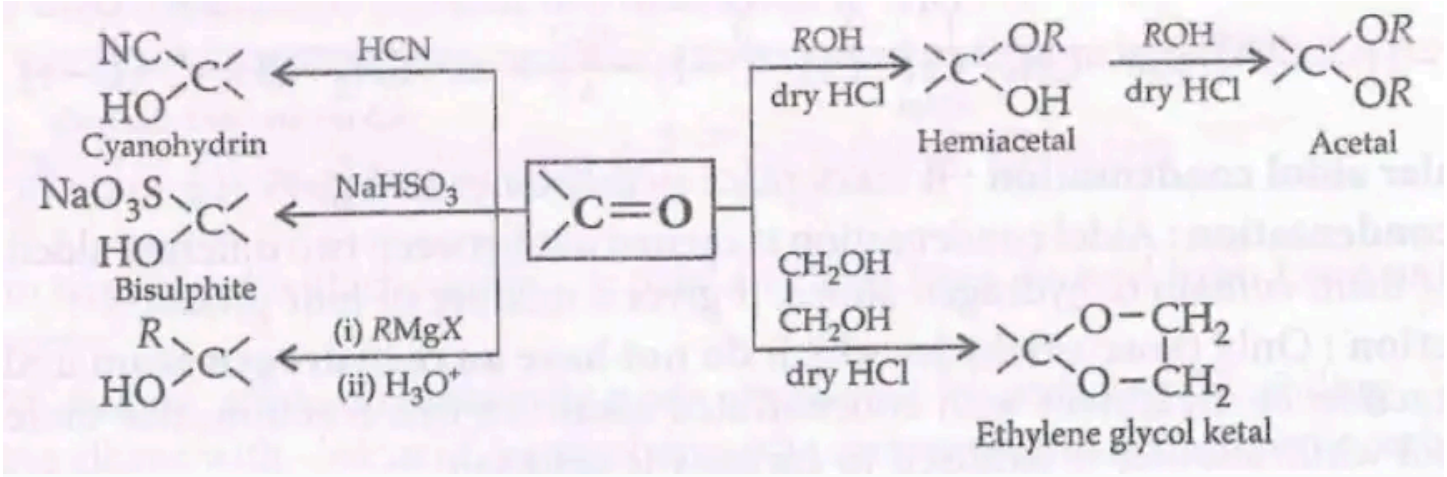
C–Nu

O–H

Bonds broken

C–O (π)

Reaction	Nucleophile	Product
Reaction with Grignard reagent (*R*–Mg*X*)	R^-	HO, H, *R*, *R*
Addition of organolithium (*R*–Li)	R^-	HO, H, *R*, *R*
Reduction by sodium borohydride ($NaBH_4$)	H^-	HO, H, *R*, H
Reduction by lithium aluminium hydride ($LiAlH_4$)	H^-	HO, H, *R*, H
Addition of cyanide ion to form cyanohydrins	$:\bar{C}N$	HO, H, *R*, CN
Addition of hydroxide ion to form hydrates	$:\ddot{O}H^-$	HO, H, *R*, OH
Addition of alkoxide ions to form hemiacetals	$:\ddot{O}R^-$	HO, H, *R*, OR



Solved Examples

- Ex 1: Reaction of aldehyde with HCN.
  - HCN adds to carbonyl carbon forming cyanohydrin.
- Ex 2: Formation of hemiacetal from aldehyde and alcohol in acidic medium.
  - Alcohol attacks carbonyl carbon, followed by protonation.

Practice Set

- Q1: Which reagent forms cyanohydrin with aldehydes?
  - A. $NaHSO_3$
  - B. HCN
  - C. RMgX
  - D. ROH
- Q2: Why are aldehydes more reactive than ketones in nucleophilic addition?
  - A. More steric hindrance in aldehydes
  - B. Less steric hindrance and electronic effects
  - C. Aldehydes are less polar
  - D. Ketones have no carbonyl group
- Q3: Which product forms when aldehyde reacts with $NaHSO_3$?
  - A. Cyanohydrin
  - B. Bisulphite addition compound
  - C. Hemiacetal
  - D. Acetal

Answer Key

- Q1: B - HCN adds to carbonyl carbon forming cyanohydrin.
- Q2: B - Aldehydes have less steric hindrance and more electrophilicity.
- Q3: B - $NaHSO_3$ forms bisulphite addition compound.

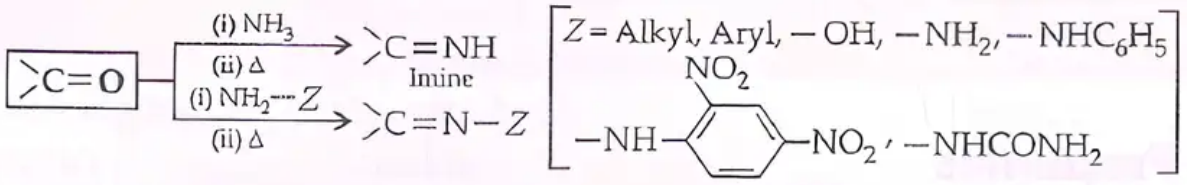
Memory Aids

- Aldehydes > Ketones in reactivity due to sterics.
- Common nucleophiles: HCN, RMgX, ROH, $NaHSO_3$.
- Nucleophilic addition breaks C=O double bond forming alcohol derivatives.

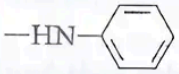
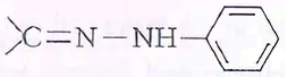
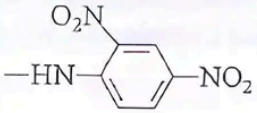
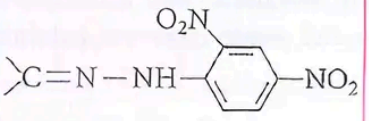
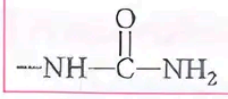
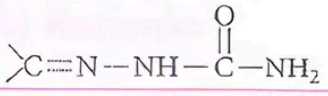
Nucleophilic Addition-Elimination Reactions

Explanation

- Carbonyl compounds react with nitrogen nucleophiles (NH_3, amines) to form imines or Schiff bases.
- Reaction involves nucleophilic attack, elimination of water, and formation of C=N bond.
- Different nitrogen reagents form imines, oximes, hydrazones, semicarbazones.
- Useful for identification and characterization of aldehydes and ketones.



Some N-substituted derivatives of aldehydes and ketones (>C=N−Z)

Z	Reagent name	Carbonyl derivative	Product name
−H	Ammonia	>C=NH	Imine
−R	Amine	>C=NR	Substituted imine (Schiff's base)
−OH	Hydroxylamine	>C=N−OH	Oxime
$-NH_2$	Hydrazine	>C=N−NH_2	Hydrazone
	Phenylhydrazine		Phenylhydrazone
	2, 4-Dinitrophenyl-hydrazine		2, 4-Dinitrophenylhydrazone
	Semicarbazide		Semicarbazone

Solved Examples

- Ex 1: Formation of imine from aldehyde and ammonia.
  - Ammonia attacks carbonyl carbon.
  - Water eliminated forming C=NH (imine).
- Ex 2: Formation of oxime from aldehyde and hydroxylamine.
  - Hydroxylamine reacts with carbonyl to form C=NOH (oxime).

Practice Set

- Q1: What product forms when aldehyde reacts with NH_3 and heat?
  - A. Oxime
  - B. Hydrazone
  - C. Imine
  - D. Semicarbazone
- Q2: Which reagent forms hydrazone derivatives?
  - A. Hydroxylamine
  - B. Hydrazine
  - C. Semicarbazide
  - D. Ammonia
- Q3: What is the key bond formed in Schiff bases?
  - A. C=O
  - B. C=N
  - C. C-C
  - D. C-H

Answer Key

- Q1: C - Imine (C=NH) forms with ammonia and heat.
- Q2: B - Hydrazine forms hydrazone derivatives.
- Q3: B - Schiff bases have C=N bond.

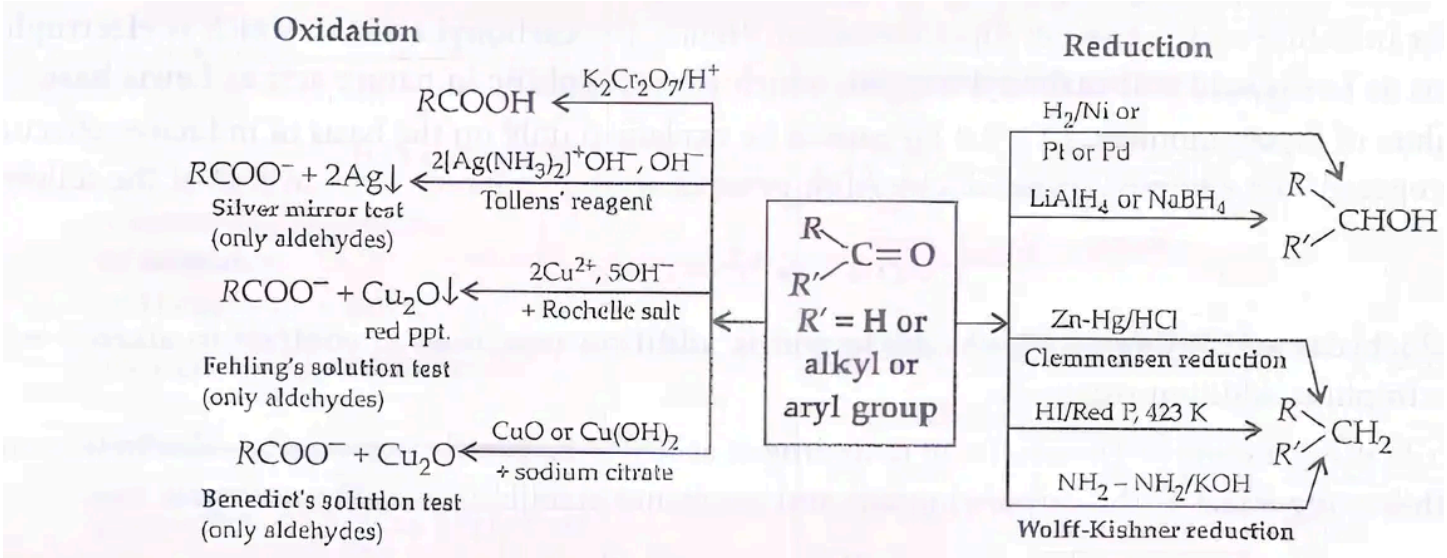
Memory Aids

- Imine = C=NH from NH_3.
- Oxime = C=NOH from hydroxylamine.
- Hydrazone = $C=NNH_2$ from hydrazine.
- Semicarbazone = from semicarbazide.

Oxidation and Reduction Reactions

Explanation

- Aldehydes oxidize to carboxylic acids using $K_2Cr_2O_7$, Tollens' reagent.
- Tollens' test: silver mirror forms with aldehydes.
- Fehling's and Benedict's tests: red precipitate with aldehydes.
- Reduction of aldehydes and ketones to alcohols using H_2/Ni, Pt, Pd or $LiAlH_4$, $NaBH_4$.
- Further reduction of aldehydes to hydrocarbons by Clemmensen or Wolff-Kishner reductions.



Solved Examples

- Ex 1: Oxidation of aldehyde with Tollens' reagent.
  - Aldehyde oxidized to acid, silver mirror formed.
- Ex 2: Reduction of ketone with $NaBH_4$.
  - Ketone reduced to secondary alcohol.

Practice Set

- Q1: Which reagent oxidizes aldehydes to acids?
  - A. $NaBH_4$
  - B. $K_2Cr_2O_7$
  - C. $LiAlH_4$
  - D. H_2/Ni
- Q2: What is the product of reduction of ketone with $NaBH_4$?
  - A. Primary alcohol
  - B. Secondary alcohol
  - C. Hydrocarbon
  - D. Carboxylic acid
- Q3: Which test produces silver mirror with aldehydes?
  - A. Fehling's test
  - B. Benedict's test
  - C. Tollens' test
  - D. 2,4-DNP test

Answer Key

- Q1: B - $K_2Cr_2O_7$ oxidizes aldehydes to acids.
- Q2: B - Ketones reduce to secondary alcohols with $NaBH_4$.
- Q3: C - Tollens' test forms silver mirror with aldehydes.

Memory Aids

- Tollens' test: silver mirror for aldehydes.
- Fehling's/Benedict's: red precipitate for aldehydes.
- $NaBH_4$/$LiAlH_4$ reduce carbonyl to alcohol.

Haloform Reaction

Explanation

- Occurs with compounds having $CH_3CO—$ or $CH_3CH(OH)—$ groups.
- Reaction with NaOH and halogen (I_2) produces haloform (CHI_3) and carboxylate salt.
- Used as a test for methyl ketones and related compounds.

$$2NaOH + I_2 \longrightarrow NaI + NaOI + H_2O$$

$$RCOCH_3 + 3NaOI \longrightarrow RCOONa + \underset{\substack{\text{Iodoform}\\(\text{yellow ppt.})}}{CHI_3\downarrow} + 2NaOH$$

Solved Examples

- Ex 1: Iodoform test with methyl ketone.
  - NaOH + I_2 forms NaOI.
  - Methyl ketone reacts with NaOI to give CHI_3 (yellow precipitate) and RCOONa.

Practice Set

- Q1: Which group is necessary for haloform reaction?
  - A. $CH_3CO—$
  - B. CH_2OH
  - C. COOH
  - D. OH
- Q2: What is the haloform produced in iodoform test?
  - A. $CHCl_3$
  - B. $CHBr_3$
  - C. CHI_3
  - D. CHF_3
- Q3: What is the color of iodoform precipitate?
  - A. White
  - B. Yellow
  - C. Orange
  - D. Red

Answer Key

- Q1: A - $CH_3CO—$ group is required.
- Q2: C - Iodoform (CHI_3) is produced.
- Q3: B - Iodoform precipitate is yellow.

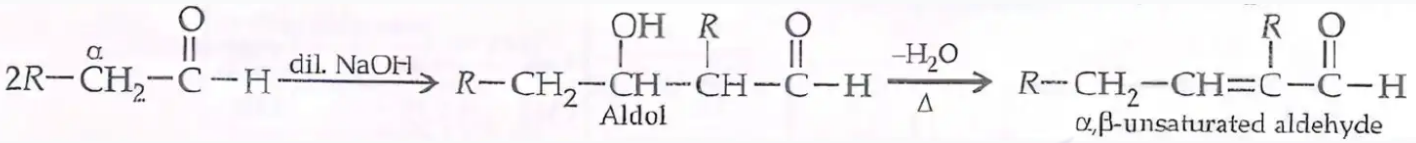
Memory Aids

- Haloform reaction = methyl ketones + halogen + base.
- Iodoform test gives yellow CHI_3 precipitate.

Aldol Condensation

Explanation

- Aldehydes/ketones with at least one α-hydrogen react in dilute alkali to form β-hydroxy aldehydes (aldol) or ketones (ketol).
- These β-hydroxy compounds dehydrate on heating to form α,β-unsaturated carbonyl compounds.
- Intramolecular aldol condensation occurs in diketones forming cyclic products.
- Cross aldol condensation between two different carbonyl compounds with α-hydrogens gives mixture of products.



Solved Examples

- Ex 1: Aldol condensation of acetaldehyde.
  - Two acetaldehyde molecules react in NaOH to form aldol.
  - Heating causes dehydration to α,β-unsaturated aldehyde.

Practice Set

- Q1: What is the product of aldol condensation before dehydration?
  - A. α,β-unsaturated aldehyde
  - B. β-hydroxy aldehyde
  - C. Ketone
  - D. Alcohol
- Q2: Intramolecular aldol condensation occurs in?
  - A. Monoketones
  - B. Diketones
  - C. Alcohols
  - D. Aldehydes without α-H
- Q3: Cross aldol condensation between two aldehydes with α-H gives?
  - A. Single product
  - B. Mixture of four products

- C. No reaction
- D. Only ketones

Answer Key

- Q1: B - β-hydroxy aldehyde is formed initially.
- Q2: B - Diketones undergo intramolecular aldol condensation.
- Q3: B - Mixture of four products formed.

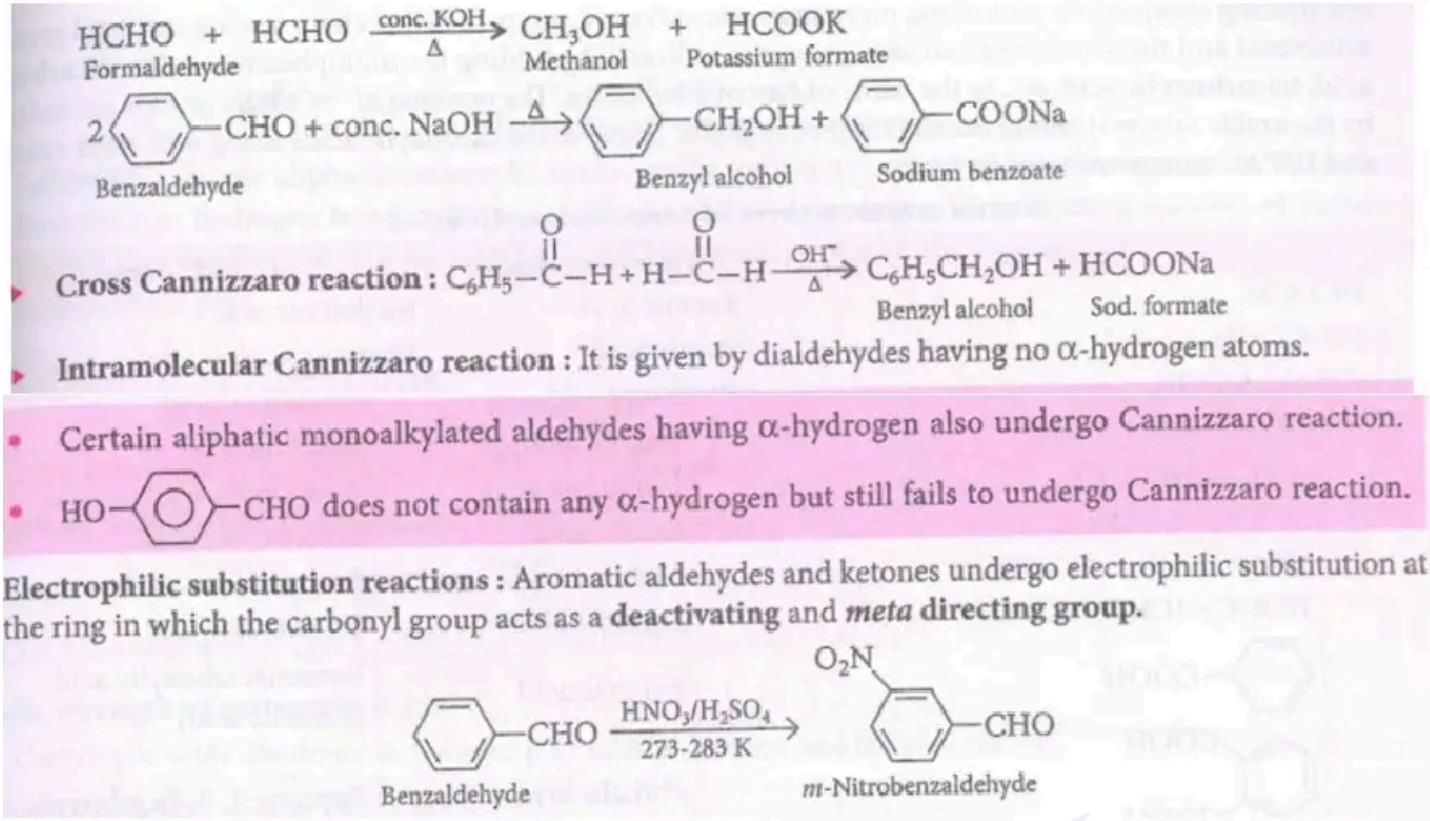
Memory Aids

- Aldol = β-hydroxy aldehyde/ketone.
- Dehydration leads to α,β-unsaturated carbonyl.
- Intramolecular = cyclic products from diketones.

Cannizzaro Reaction

Explanation

- Aldehydes without α-hydrogen undergo self-oxidation and reduction with concentrated alkali.
- One molecule reduces to alcohol, another oxidizes to carboxylate salt.
- Cross and intramolecular Cannizzaro reactions also occur.
- Aromatic aldehydes undergo electrophilic substitution reactions.



Solved Examples

- Ex 1: Cannizzaro reaction of benzaldehyde.
  - Benzaldehyde reacts with concentrated NaOH to give benzyl alcohol and sodium benzoate.

Practice Set

- Q1: Which aldehydes undergo Cannizzaro reaction?
  - A. With α-hydrogen
  - B. Without α-hydrogen
  - C. All aldehydes
  - D. Only aromatic aldehydes
- Q2: Products of Cannizzaro reaction are?
  - A. Two alcohols
  - B. Alcohol and carboxylate salt
  - C. Two acids
  - D. Alcohol and ketone
- Q3: Cannizzaro reaction requires?
  - A. Dilute acid

- B. Concentrated alkali
- C. Heat only
- D. Catalyst

Answer Key

- Q1: B - Aldehydes without α-hydrogen undergo Cannizzaro reaction.
- Q2: B - Alcohol and carboxylate salt are formed.
- Q3: B - Concentrated alkali is required.

Memory Aids

- Cannizzaro: Aldehydes without α-H, base, self redox.
- One molecule oxidized, one reduced.
- Aromatic aldehydes undergo electrophilic substitution.

Distinction Between Aldehydes and Ketones

Explanation

- Schiff’s reagent: Aldehydes turn pink; ketones no change.
- Fehling’s and Benedict’s tests: Aldehydes give red precipitate; ketones do not.
- Tollens’ reagent: Aldehydes form silver mirror; ketones do not.
- 2,4-Dinitrophenylhydrazine: Both form colored crystals with specific melting points.
- α-Hydroxy ketones reduce Tollens’, Fehling’s, and Benedict’s solutions.
- Haloform reaction oxidizes α,β-unsaturated methyl ketones to acids without affecting double bond.

Tests with	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red precipitate	No precipitate
Tollens' reagent	Silver mirror	No silver mirror
2,4-Dinitrophenyl-hydrazine	Orange-yellow or red well defined crystals with melting points characteristic of individual aldehydes.	Orange-yellow or red well defined crystals with melting points characteristic of individual ketones.

Solved Examples

- Ex 1: Test to distinguish aldehyde and ketone using Tollens' reagent.
  - Aldehyde forms silver mirror; ketone no reaction.

Practice Set

- Q1: Which reagent gives silver mirror with aldehydes?
  - A. Fehling's solution
  - B. Tollens' reagent
  - C. 2,4-DNP
  - D. Benedict's solution
- Q2: Which test gives red precipitate with aldehydes?
  - A. Schiff's reagent
  - B. Fehling's solution
  - C. Tollens' reagent
  - D. 2,4-DNP
- Q3: Which compound reduces Tollens' reagent besides aldehydes?
  - A. Ketones
  - B. α-Hydroxy ketones
  - C. Alcohols
  - D. Carboxylic acids

Answer Key

- Q1: B - Tollens' reagent forms silver mirror with aldehydes.
- Q2: B - Fehling's solution gives red precipitate with aldehydes.

- Q3: B - α-Hydroxy ketones reduce Tollens' reagent.

Memory Aids

- Schiff's: Pink for aldehydes.
- Tollens': Silver mirror for aldehydes.
- Fehling's/Benedict's: Red precipitate for aldehydes.
- α-Hydroxy ketones behave like aldehydes in tests.

Uses of Aldehydes and Ketones

Applications in Industry

- Aldehydes and ketones serve as solvents in the chemical industry.
- Used as starting materials and reagents for synthesizing various organic compounds.
- Formalin (40% formaldehyde solution) preserves biological specimens.
- Formaldehyde is key in producing bakelite (phenol-formaldehyde resin), urea-formaldehyde glues, and other polymers.
- Acetaldehyde (CH_3CHO) is a precursor for acetic acid, ethyl acetate, vinyl acetate, polymers, and drugs.
- Benzaldehyde is utilized in perfumery and dye industries.
- Compounds like butyraldehyde, vanillin, acetophenone, and camphor are used as flavoring agents.

Solved Examples

- **Ex 1:** Identify the use of formalin in laboratories.
  - Formalin is used to preserve biological specimens due to its disinfectant and preservative properties.
- **Ex 2:** Name the polymer formed from formaldehyde and phenol.
  - Bakelite, a phenol-formaldehyde resin, is synthesized using formaldehyde and phenol.

Practice Set

- **Q1:** Which aldehyde is used as a starting material for acetic acid production?
  A. Benzaldehyde
  B. Acetaldehyde
  C. Formaldehyde
  D. Butyraldehyde
- **Q2:** Formaldehyde is NOT used in which of the following?
  A. Preserving biological specimens
  B. Synthesis of bakelite
  C. Manufacture of ethyl acetate
  D. Flavoring agents
- **Q3:** Which compound is commonly used in perfumery and dye industries?
  A. Acetophenone
  B. Benzaldehyde
  C. Vanillin
  D. Camphor

Answer Key

- **Q1:** B. Acetaldehyde - It is the precursor for acetic acid and related compounds.
- **Q2:** D. Flavoring agents - Formaldehyde is not used as a flavoring agent.
- **Q3:** B. Benzaldehyde - Widely used in perfumery and dye industries.

Memory Aids

- Formalin = Formaldehyde + Water (40%) → Preserves specimens.
- Bakelite = Phenol + Formaldehyde → Polymer resin.
- Acetaldehyde → Acetic acid, esters, polymers.
- Benzaldehyde → Perfumes and dyes.
- Flavor agents: Butyraldehyde, vanillin, acetophenone, camphor.

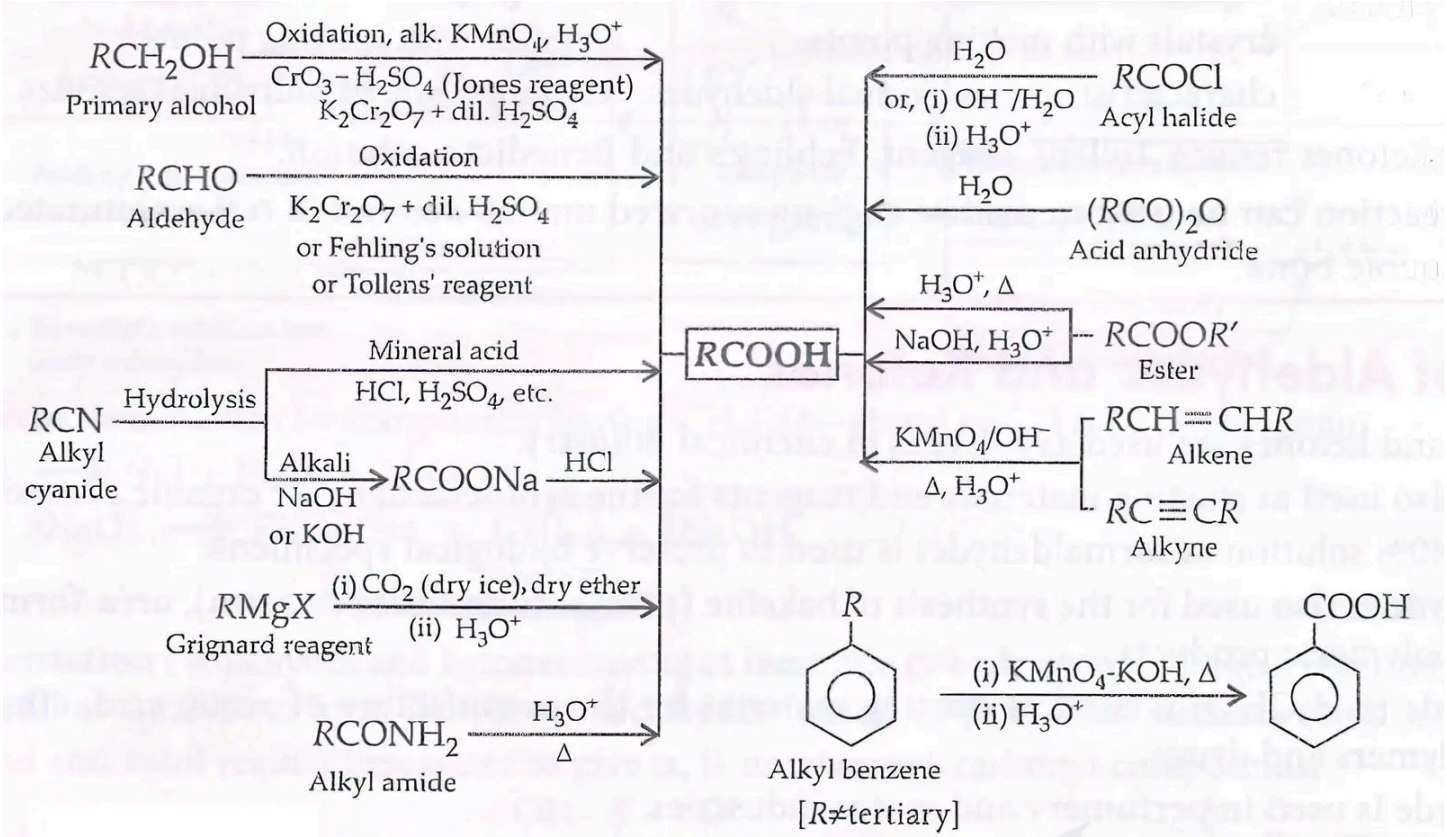
Methods of Preparation of Carboxylic Acids

Overview

- Carboxylic acids (RCOOH) can be prepared from various organic compounds by specific chemical reactions.
- Common starting materials include primary alcohols, aldehydes, alkyl cyanides, Grignard reagents, amides, alkenes, alkynes, acyl halides, acid anhydrides, and esters.
- Oxidation, hydrolysis, and substitution reactions are key methods used.
- Aromatic alkyl groups can be oxidized to carboxylic acids using strong oxidizers.

Preparation Routes

- **From Primary Alcohols:** Oxidation using $KMnO_4$ or Cr reagents converts RCH_2OH to RCOOH.
- **From Aldehydes:** Oxidation of RCHO to RCOOH using strong oxidizing agents.
- **From Alkyl Cyanides (RCN):** Hydrolysis under acidic or basic conditions yields RCOOH.
- **From Grignard Reagents:** Reaction with CO_2 followed by acid work-up forms RCOOH.
- **From Amides:** Hydrolysis of $RCONH_2$ under acidic or basic conditions produces RCOOH.
- **From Alkenes and Alkynes:** Oxidative cleavage with $KMnO_4$ or ozone leads to carboxylic acids.
- **From Acyl Halides, Acid Anhydrides, and Esters:** Hydrolysis or reaction with water/acid/base regenerates RCOOH.
- **From Alkyl Benzene:** Side chain oxidation with strong oxidizers converts alkyl groups to carboxylic acids.



Solved Examples

- **Ex 1:** Convert ethanol (CH_3CH_2OH) to ethanoic acid (CH_3COOH).
  - Step 1: Oxidize ethanol with $KMnO_4$.
  - Step 2: Ethanol → ethanal → ethanoic acid.
- **Ex 2:** Prepare benzoic acid from toluene.
  - Step 1: Oxidize toluene with $KMnO_4$ under reflux.
  - Step 2: Side chain oxidized to carboxyl group forming benzoic acid.

Practice Set

- **Q1:** Which reagent is used to oxidize primary alcohols to carboxylic acids?
  - A. $NaBH_4$
  - B. $KMnO_4$
  - C. $LiAlH_4$
  - D. H_2SO_4
- **Q2:** Hydrolysis of alkyl cyanides yields:
  - A. Alcohols
  - B. Aldehydes
  - C. Carboxylic acids

    - D. Ketones
- **Q3:** Which starting material reacts with CO_2 in the presence of acid to form carboxylic acid?
    - A. Alkyl halide
    - B. Grignard reagent
    - C. Alkene
    - D. Ester

Answer Key

- **Q1:** B. $KMnO_4$ - Strong oxidizer converting primary alcohols to carboxylic acids.
- **Q2:** C. Carboxylic acids - Hydrolysis of RCN yields RCOOH.
- **Q3:** B. Grignard reagent - Reacts with CO_2 to form carboxylate intermediate, acidified to RCOOH.

Memory Aids

- Primary alcohols and aldehydes → oxidize with $KMnO_4$ or Cr reagents to carboxylic acids.
- Alkyl cyanides → hydrolyze to carboxylic acids.
- Grignard reagents + CO_2 → carboxylic acids after acid work-up.
- Alkyl benzene side chains → oxidized to benzoic acid derivatives.

Physical Properties

Physical State

- Lower fatty acids (up to C_9) are colourless liquids.
- Higher fatty acids are colourless waxy solids.

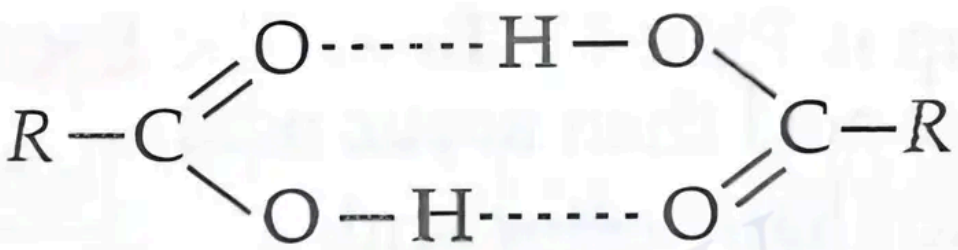
Odour

- First three members have a sharp pungent odour.
- Members from C_4 to C_9 smell like rancid butter.

- Higher members have no smell.

Boiling Points

- Carboxylic acids have higher boiling points than aldehydes, ketones, and alcohols of similar molecular mass.
- Due to strong intermolecular hydrogen bonding, molecules associate extensively.
- Hydrogen bonds persist even in the vapour phase.



Exists as dimer in vapour state or in aprotic solvent

This image shows a dimer formed by two carboxylic acid molecules connected through hydrogen bonds:

- Each molecule has a carboxyl group (R-COOH).
- Hydrogen bonds form between the hydrogen of one -OH and the oxygen of the other's C=O group.
- This creates a stable ring-like dimer structure.
- Dimers are common in vapor state or aprotic solvents.
- Dotted lines represent hydrogen bonds.

Solubility

- Simple aliphatic carboxylic acids (up to 4 carbons) are miscible with water due to hydrogen bonding.
- Solubility decreases as carbon chain length increases.
- Higher carboxylic acids are practically insoluble due to hydrophobic hydrocarbon chains.

Solved Examples

- **Ex 1:** Explain why acetic acid has a higher boiling point than ethanol.
  - Acetic acid forms dimers via hydrogen bonding.
  - Ethanol forms hydrogen bonds but no dimerization.
  - Dimerization increases intermolecular forces, raising boiling point.
- **Ex 2:** Predict solubility of hexanoic acid in water.
  - Hexanoic acid has 6 carbons.
  - Solubility decreases beyond 4 carbons.
  - Hence, hexanoic acid is sparingly soluble.

Practice Set

- **Q1:** Which physical state is typical for octanoic acid?
  A. Colourless liquid
  B. Colourless waxy solid
  C. Coloured liquid
  D. Coloured solid
- **Q2:** What causes the high boiling point of carboxylic acids?
  A. Ionic bonding
  B. Van der Waals forces
  C. Intermolecular hydrogen bonding and dimer formation
  D. Dipole-dipole interactions
- **Q3:** Which carboxylic acid is most soluble in water?
  A. Butanoic acid (C_4)
  B. Hexanoic acid (C_6)
  C. Octanoic acid (C_8)
  D. Decanoic acid (C_{10})

Answer Key

- **Q1:** B - Octanoic acid (C_8) is a higher fatty acid and exists as a colourless waxy solid.
- **Q2:** C - Carboxylic acids form strong intermolecular hydrogen bonds and dimers, increasing boiling points.
- **Q3:** A - Butanoic acid (C_4) is miscible in water due to hydrogen bonding; solubility decreases with chain length.

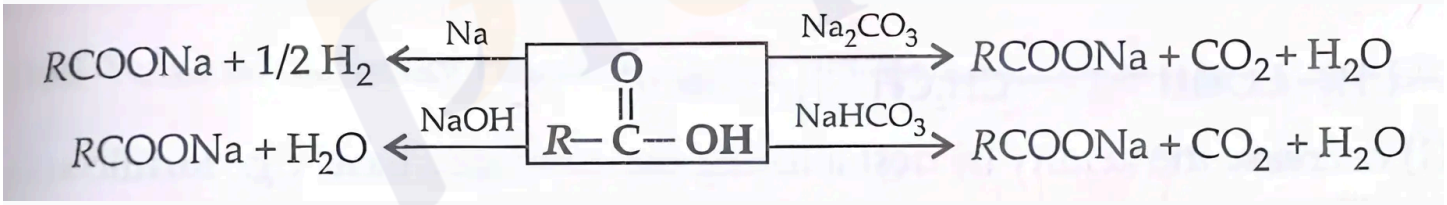
Memory Aids

- "Up to C4, soluble; beyond, insoluble" for carboxylic acids in water.
- Remember dimer formation increases boiling points.
- Odour changes: sharp pungent (C1-C3), rancid butter (C4-C9), no smell (higher).

Reactions Involving Cleavage of O — H Bond

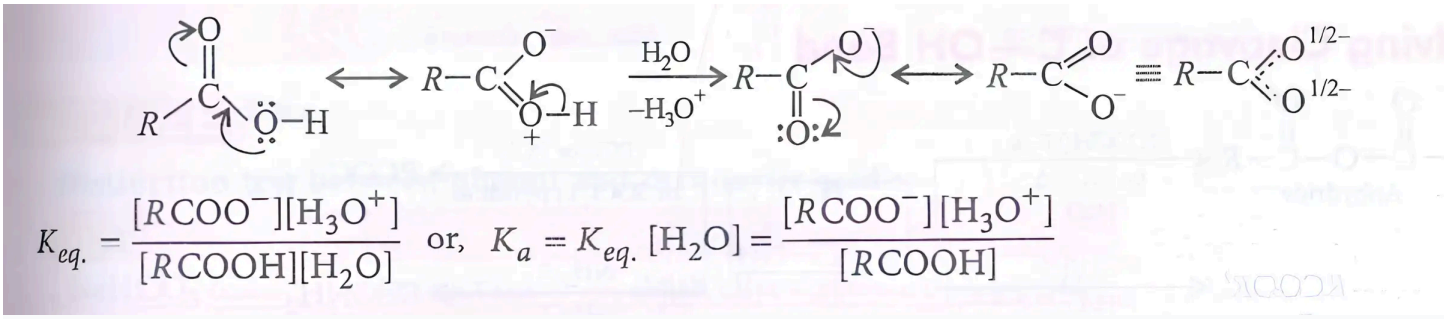
Reactions with metals and alkalies

- Carboxylic acid (R-COOH) reacts with sodium (Na) to form sodium salt (RCOONa) and hydrogen gas (H_2).
- Sodium salt (RCOONa) reacts with sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$) to produce CO_2, H_2O, and regenerate sodium salt.
- Sodium salt reacts with water and sodium hydroxide (NaOH) to revert back to carboxylic acid.
- These reactions demonstrate acid-base behavior and salt formation of carboxylic acids.

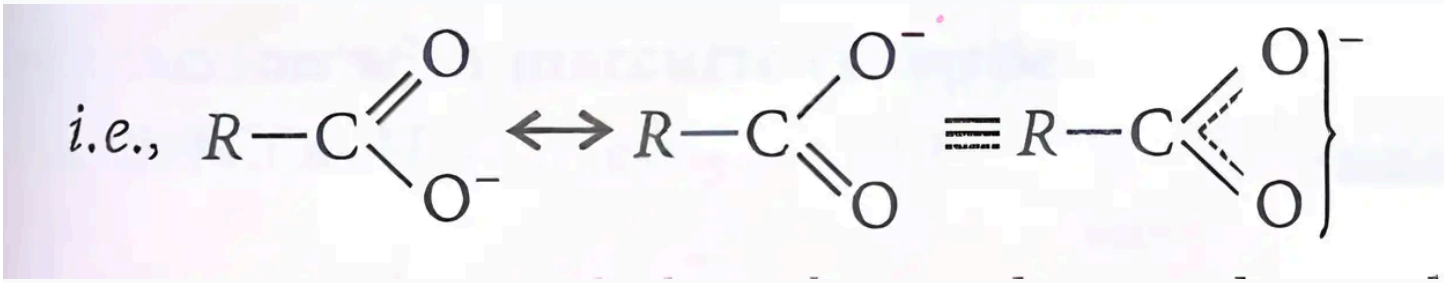


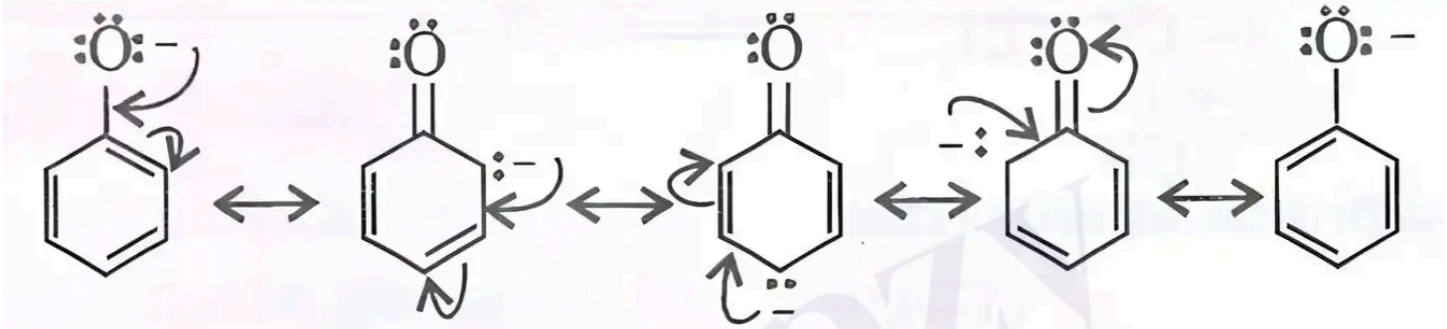
Acidic strength of carboxylic acids

- Carboxylic acids dissociate in water: $RCOOH + H_2O \rightarrow RCOO^- + H_3O^+$.
- Acidity due to positive charge on oxygen liberating proton; carboxylate ion is resonance stabilized.
- Equilibrium constant (K_{eq}) and acid dissociation constant (K_a) describe acid strength.
- $pK_a = -\log K_a$; acidity $\propto 1/pK_a$.
- Carboxylic acids are weaker than mineral acids but stronger than phenols and alcohols.
- Carboxylate ion has two equivalent resonance structures with negative charge on electronegative oxygen, making it more stable than phenoxide ion.



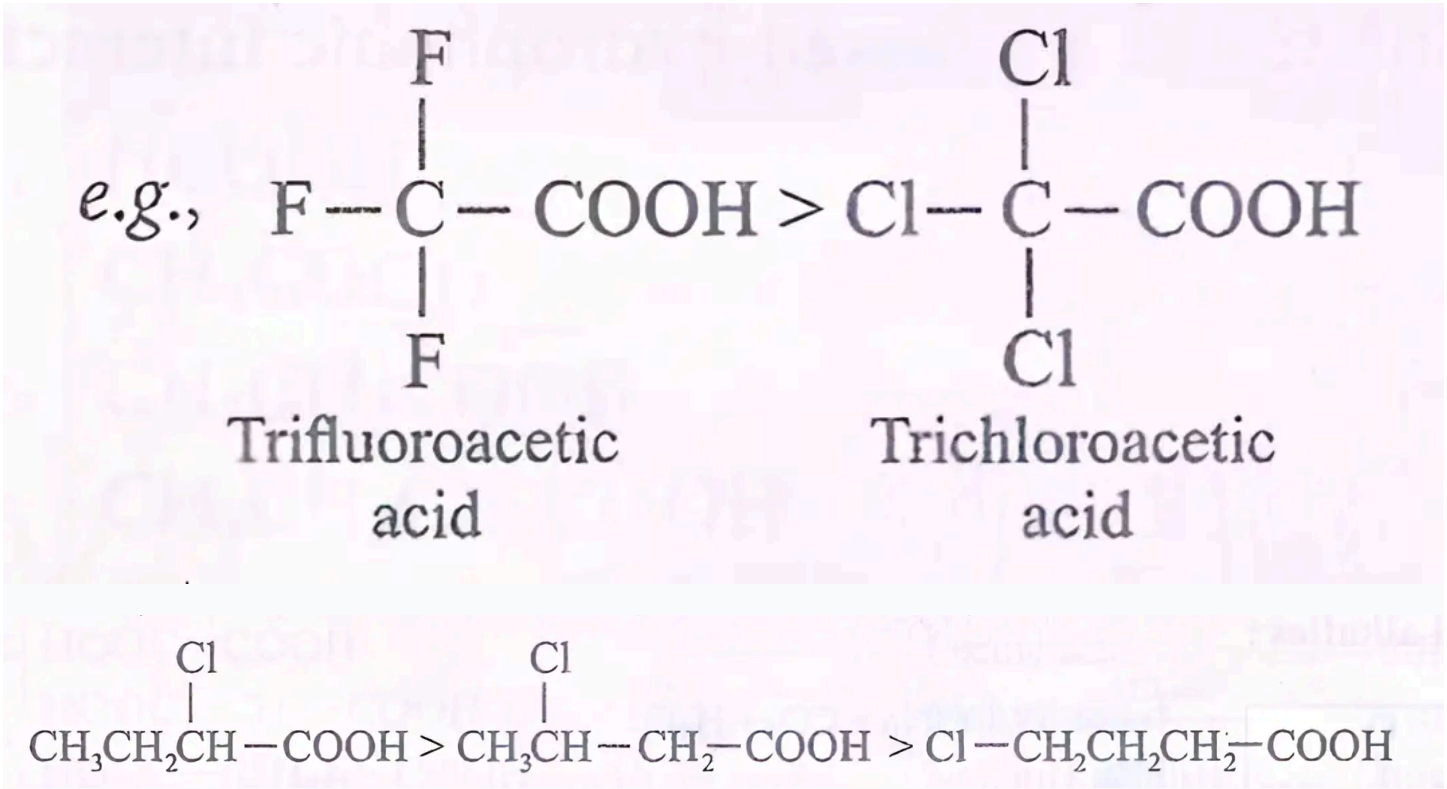
$$K_{eq.} = \frac{[RCOO^-][H_3O^+]}{[RCOOH][H_2O]} \quad \text{or,} \quad K_a = K_{eq.}[H_2O] = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$





Effect of substituents on acidity

- Electron withdrawing groups (EWG) increase acidity by stabilizing conjugate base via inductive/resonance effects.
- Acidity order: Ph < I < Br < Cl < F < CN < NO_2 < CF_3.
- Examples: Chloroacetic acid > Acetic acid; Benzoic acid > Acetic acid.
- Acidity increases with number of EWGs: Trichloroacetic acid > Dichloroacetic acid > Chloroacetic acid > Acetic acid.
- Acidity increases with electronegativity of substituents.
- Acidity increases with decreasing distance of halogen from COOH group.
- Electron donating groups (EDG) decrease acidity by destabilizing conjugate base; e.g., Formic acid > Acetic acid.
- Aromatic acids: EWG on phenyl ring increase acidity (p-nitrobenzoic acid > benzoic acid); EDG decrease acidity (p-methoxybenzoic acid < benzoic acid).



Solved Examples

- **Ex 1:** Compare acidity of trifluoroacetic acid and trichloroacetic acid.
  Answer: Trifluoroacetic acid is stronger due to higher electronegativity of F than Cl.
- **Ex 2:** Predict product when chloroacetic acid reacts with NaOH.
  Answer: Sodium chloroacetate (RCOONa) salt forms.

Practice Set

- Q1: Which is the strongest acid?
  A. Acetic acid
  B. Chloroacetic acid
  C. Benzoic acid
  D. Formic acid
- Q2: What happens when sodium salt of carboxylic acid reacts with $NaHCO_3$?
  A. No reaction
  B. CO_2 and H_2O formed
  C. H_2 gas evolved
  D. Salt precipitates
- Q3: Which substituent increases acidity the most?
  A. -OH

B. -NO_2

C. -CH_3

D. -OCH_3

Answer Key

- Q1: B - Chloroacetic acid is stronger due to electron withdrawing Cl group.
- Q2: B - Reaction with $NaHCO_3$ produces CO_2 and H_2O.
- Q3: B - Nitro group (-NO_2) is a strong electron withdrawing group increasing acidity.

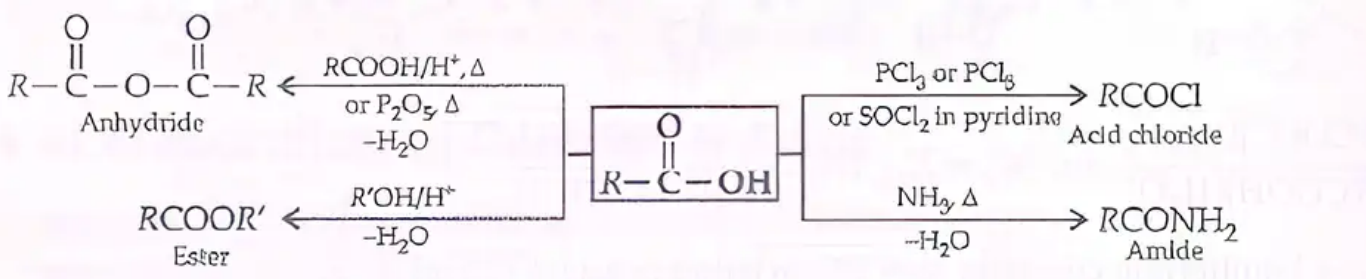
Memory Aids

- EWG increase acidity; EDG decrease acidity.
- Acidity order: Ph < I < Br < Cl < F < CN < NO_2 < CF_3.
- Closer halogen to COOH, stronger acid.
- Carboxylate ion resonance stabilizes conjugate base.

Reactions Involving Cleavage of C—OH Bond

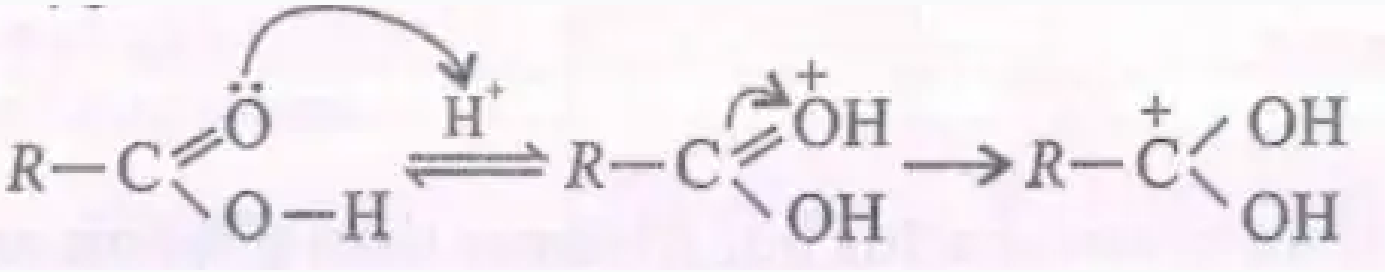
Derivatives formation from carboxylic acid

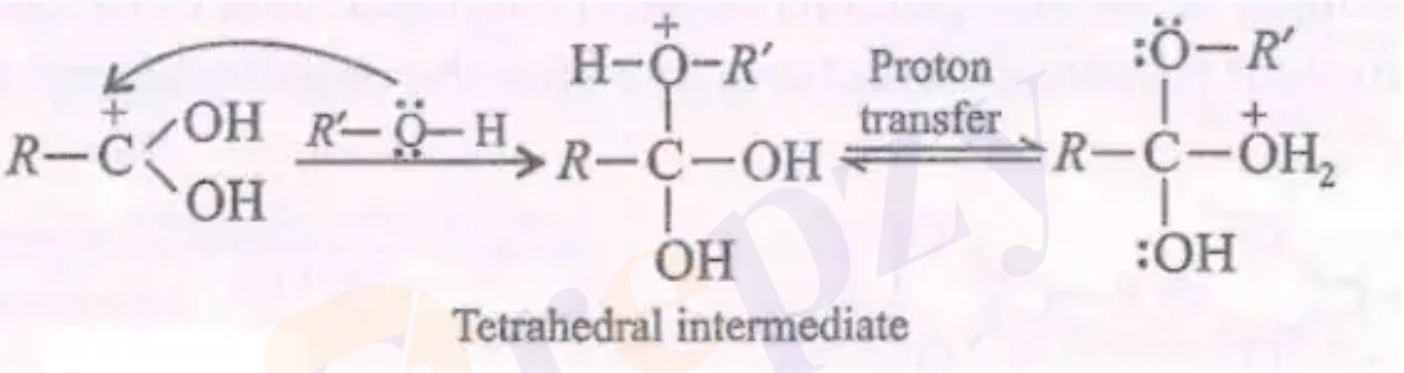
- Carboxylic acid (R-COOH) reacts to form:
  - Acid anhydrides: React with acid and heat, removing water.
  - Esters: React with alcohol (R'OH) and acid catalyst, removing water.
  - Acid chlorides: React with PCl_3 or $SOCl_2$ in pyridine.
  - Amides: React with NH_3 and heat, removing water.

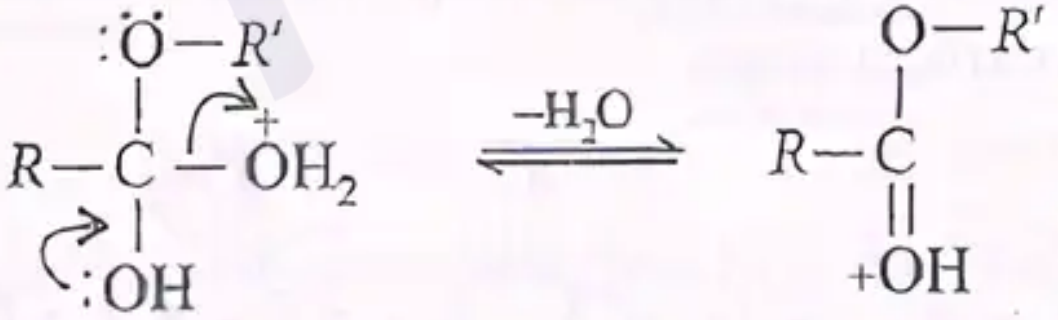


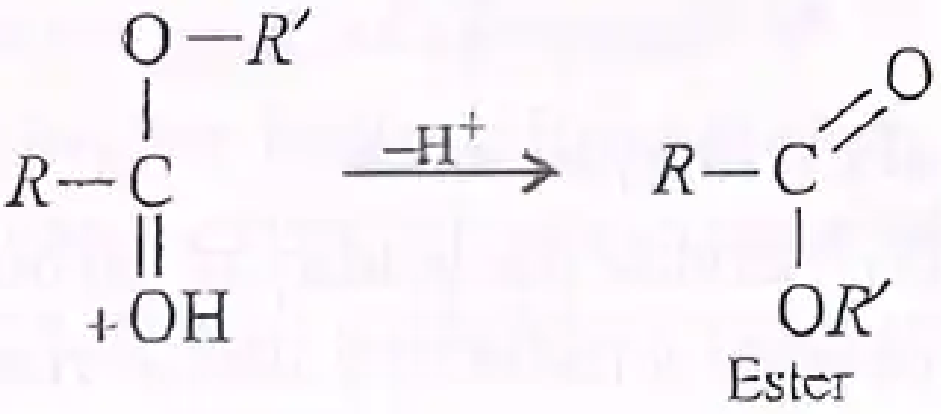
Mechanism of esterification

- Nucleophilic acyl substitution.
- (a) Protonation of carboxyl oxygen by acid (H^+).
- (b) Nucleophilic addition of alcohol to carbonyl carbon forming tetrahedral intermediate.
- (c) Elimination of water molecule forming carbocation intermediate.
- (d) Protonated ester loses proton to give ester.









Solved Examples

- **Ex 1:** Write the product of esterification of acetic acid with methanol.
  Answer: Methyl acetate (CH_3COOCH_3).
- **Ex 2:** Identify the intermediate formed after nucleophilic addition in esterification.
  Answer: Tetrahedral intermediate.

Practice Set

- Q1: Which reagent converts carboxylic acid to acid chloride?
  A. PCl_3
  B. NaOH
  C. NH_3
  D. Alcohol
- Q2: What is the role of acid in esterification?
  A. Nucleophile
  B. Catalyst and protonates carbonyl oxygen
  C. Base
  D. Reducing agent
- Q3: What intermediate is formed after nucleophilic addition of alcohol?
  A. Carbocation
  B. Tetrahedral intermediate
  C. Carbene
  D. Free radical

Answer Key

- Q1: A - PCl_3 converts acid to acid chloride.
- Q2: B - Acid acts as catalyst and protonates carbonyl oxygen.
- Q3: B - Tetrahedral intermediate forms after nucleophilic addition.

Memory Aids

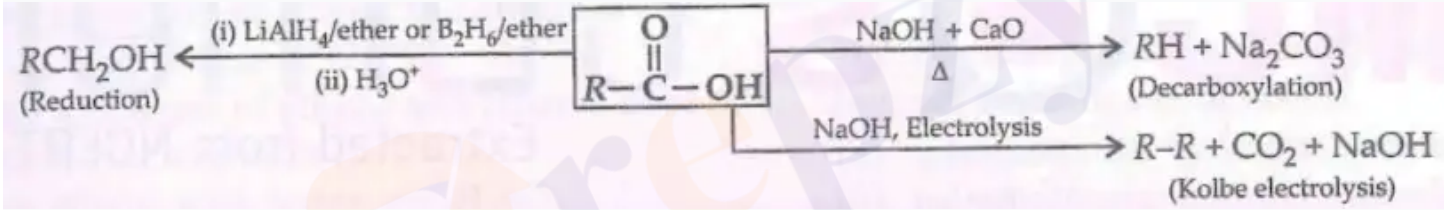
- Esterification is nucleophilic acyl substitution.

- Protonation of carbonyl oxygen activates acid.
- Tetrahedral intermediate is key step.
- Water elimination forms ester.

Reactions Involving COOH Group

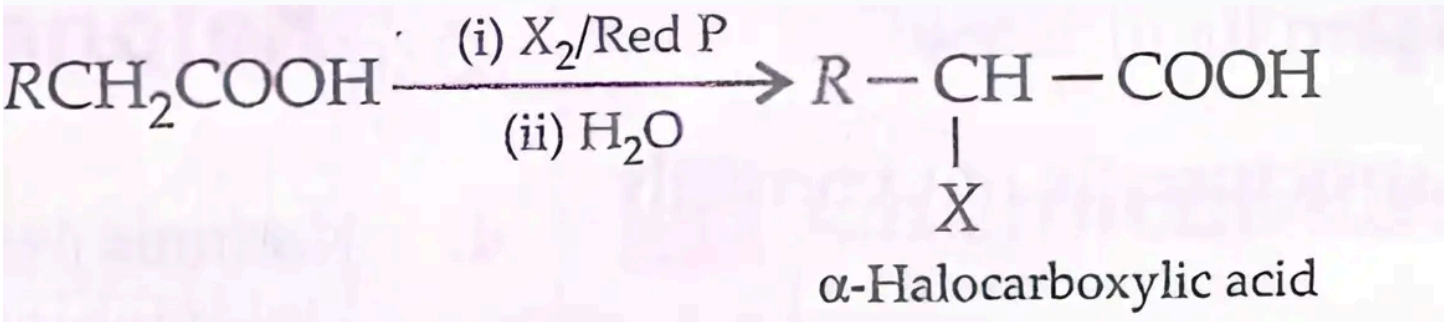
Reduction, decarboxylation, and electrolysis

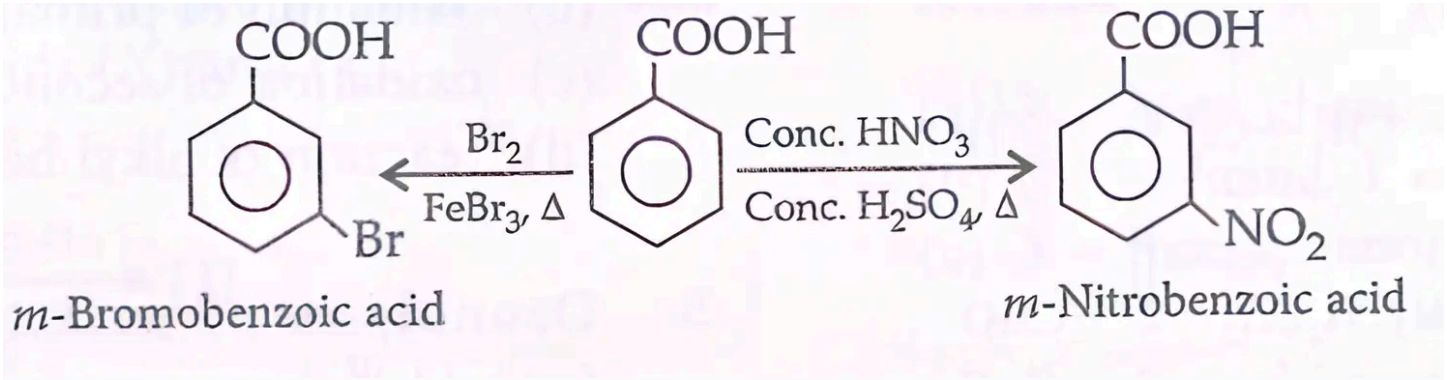
- Reduction: R–COOH → RCH_2OH using $LiAlH_4$ or B_2H_6 followed by acid workup.
- Decarboxylation: R–COOH heated with NaOH and CaO → RH + CO_2 + Na_2CO_3.
- Kolbe electrolysis: Carboxylic acid salts + NaOH + electricity → R–R + CO_2 + NaOH.
- $LiAlH_4$ is stronger reducing agent than $NaBH_4$, reducing more functional groups.
- In α,β-unsaturated aldehydes/ketones, $LiAlH_4$ reduces only C=O; $NaBH_4$ reduces both C=O and C=C but C=O reduction predominates.



Substitution reactions in hydrocarbon part

- Hell-Volhard-Zelinsky reaction: $RCH_2COOH + X_2$/Red P → α-halocarboxylic acid + H_2O.
- Ring substitution in aromatic acids: COOH group is deactivating and meta-directing in electrophilic substitution.
- Example: Benzoic acid nitration and bromination give m-nitrobenzoic acid and m-bromobenzoic acid.





Distinction test between phenol and carboxylic acid

- $NaHCO_3$ test: Phenol no reaction; Carboxylic acid effervesces CO_2.
- $FeCl_3$ test: Phenol gives violet color; Carboxylic acid gives buff precipitate.

Test	Phenol	Carboxylic acid
$NaHCO_3$ test	No reaction	Brisk effervescence of CO_2 gas.
$FeCl_3$ test	Violet colour	Buff coloured ppt.

Abnormal behaviour of formic acid

- Due to aldehydic group presence.
- Oxidation with Tollens' or Fehling's solution: Reduces them forming silver mirror or red ppt.
- Action with mercuric chloride: Forms white or grey precipitates.

Solved Examples

- **Ex 1:** Write the product of reduction of benzoic acid with $LiAlH_4$.
  Answer: Benzyl alcohol ($C_6H_5CH_2OH$).
- **Ex 2:** What is the product of Kolbe electrolysis of sodium acetate?
  Answer: Ethane (C_2H_6).

Practice Set

- Q1: Which reagent reduces carboxylic acid to alcohol?
  A. $NaBH_4$
  B. $LiAlH_4$
  C. NaOH
  D. H_2SO_4
- Q2: Hell-Volhard-Zelinsky reaction introduces halogen at which position?
  A. Beta
  B. Alpha
  C. Meta
  D. Para
- Q3: What is the product of decarboxylation of sodium benzoate?
  A. Benzene
  B. Toluene
  C. Phenol
  D. Aniline

Answer Key

- Q1: B - $LiAlH_4$ reduces carboxylic acids to alcohols.
- Q2: B - Halogen introduced at alpha position.
- Q3: B - Toluene formed by decarboxylation of sodium benzoate.

Memory Aids

- $LiAlH_4$ stronger reducer than $NaBH_4$.
- Hell-Volhard-Zelinsky: Alpha halogenation of carboxylic acids.
- COOH group meta-directing in aromatic substitution.
- Formic acid behaves like aldehyde due to -CHO group.

Uses of Carboxylic Acids

Applications of Specific Carboxylic Acids

- **Methanoic acid**: Used in rubber, textile, dyeing, leather, and electroplating industries.
- **Ethanoic acid**: Acts as a solvent and is used as vinegar in the food industry.
- **Hexanedioic acid**: Used in the manufacture of nylon-6,6 polymer.
- **Esters of benzoic acid**: Utilized in perfumery for fragrance production.
- **Sodium benzoate**: Employed as a food preservative to inhibit microbial growth.
- **Higher fatty acids**: Used in the manufacture of soaps and detergents.

Solved Examples

- **Ex 1:** Identify the carboxylic acid used in nylon production.
  - Answer: Hexanedioic acid (adipic acid) is used to make nylon-6,6.
- **Ex 2:** Which carboxylic acid is commonly used as vinegar?
  - Answer: Ethanoic acid (acetic acid) is used as vinegar in the food industry.

Practice Set

- **Q1:** Which carboxylic acid is used in electroplating?
  - A. Ethanoic acid
  - B. Methanoic acid
  - C. Hexanedioic acid
  - D. Benzoic acid
- **Q2:** Sodium benzoate is used as:
  - A. Solvent
  - B. Food preservative
  - C. Dyeing agent
  - D. Polymer
- **Q3:** Which acid is a precursor for nylon-6,6?
  - A. Methanoic acid
  - B. Ethanoic acid
  - C. Hexanedioic acid
  - D. Benzoic acid

Answer Key

- **Q1:** B. Methanoic acid - Used in electroplating and related industries.
- **Q2:** B. Food preservative - Sodium benzoate prevents microbial growth in food.
- **Q3:** C. Hexanedioic acid - It is the dicarboxylic acid used to make nylon-6,6.

Memory Aids

- Methanoic acid = Electroplating and leather industries.
- Ethanoic acid = Vinegar and solvent.
- Hexanedioic acid = Nylon-6,6 manufacture.
- Benzoic acid esters = Perfumery.
- Sodium benzoate = Food preservative.
- Higher fatty acids = Soaps and detergents.

Prepzy