Class: 12th

Subject: Chemistry

Chapter 12: ALDEHYDES AND KETONES

🩸 Keypoints Important MCQs:

1. The functional group present in aldehydes and ketones is:

(a) –OH

(b) –COOH

(c) C=O ✅

(d) $-NH_2$

2. Aldehydes are generally prepared by oxidation of:

(a) Secondary alcohols

(b) Tertiary alcohols

(c) Primary alcohols ✅

(d) Ketones

3. Ketones are generally prepared by oxidation of:

(a) Primary alcohols

(b) Secondary alcohols ✅

(c) Tertiary alcohols

(d) Aldehydes

4. The characteristic reaction of aldehydes and ketones is:

(a) Electrophilic substitution

(b) Free radical substitution

(c) Nucleophilic addition ✅

(d) Elimination reaction

5. In nucleophilic addition reactions of carbonyl compounds, the nucleophile attacks:

(a) Oxygen atom

(b) Hydrogen atom

(c) Alkyl group

(d) Electrophilic carbon of carbonyl group ✅

6. Aldol condensation occurs when:

(a) Aldehydes with no α-hydrogen react

(b) Ketones resist reaction

(c) Alcohols react with aldehydes

(d) Aldehydes or ketones with α-hydrogen react in dilute NaOH ✅

7. Cannizzaro's reaction occurs in:

(a) Aldehydes with α-hydrogen

(b) Ketones

(c) Aldehydes without α-hydrogen ✅

(d) Alcohols

8. The haloform reaction is observed in:

(a) All ketones

(b) Aldehydes with α-hydrogen

(c) Acetaldehyde and methyl ketones ✅

(d) Aromatic aldehydes

9. Iodoform test is used to distinguish:

(a) Primary alcohols from secondary alcohols

(b) Aldehydes from ketones

(c) Methyl ketones from other ketones ✅

(d) Tertiary alcohols

10. Aldehydes and ketones react with ammonia derivatives (–NH_2, –NH–G) to form:

(a) Alcohols

(b) Esters

(c) Condensation products with C=N–G ✅

(d) Ketones

11. Aldehydes and ketones can be reduced to alcohols by:

(a) $KMnO_4$

(b) H_2SO_4

(c) $NaBH_4$ or H_2 with Pd, Pt, Ni ✅

(d) Br_2

12. Aldehydes are oxidized to:

(a) Ketones

(b) Alcohols

(c) Carboxylic acids ✅

(d) Esters

13. Ketones resist oxidation because:

(a) They have α-hydrogen

(b) They form aldols easily

(c) Strong C–C bonds prevent easy oxidation ✅

(d) They reduce easily

14. Tollen's reagent gives a silver mirror with:

(a) All ketones

(b) Aldehydes ✅

(c) Alcohols

(d) Methyl ketones

15. Fehling's solution gives a brick-red precipitate with:

(a) Ketones

(b) Aliphatic aldehydes ✅

(c) Aromatic ketones

(d) Alcohols

🩸 Important MCQs:

1. The carbonyl group in aldehydes is always:

(a) Attached to two alkyl groups

(b) Present at the terminal carbon atom ✅

(c) Present at a secondary carbon atom

(d) Present in aromatic rings only

2. Which feature distinguishes aldehydes from ketones?

(a) Presence of oxygen

(b) Presence of two alkyl groups

(c) Presence of at least one hydrogen on the carbonyl carbon ✅

(d) Presence of a double bond

3. Both aldehydes and ketones have the same general molecular formula:

(a) C_nH_{2n}

(b) C_nH_{2n+2}

(c) $C_nH_{2n}O$ ✅

(d) C_nH_{2n-2}

4. The IUPAC naming of aldehydes starts numbering from:

(a) The end nearest to substituents

(b) The end nearest to the longest chain

(c) The end nearest to the carbonyl carbon

(d) The carbonyl carbon itself is carbon-1 ✅

5. Aromatic aldehydes such as benzaldehyde:

(a) Are given IUPAC names

(b) Are not given IUPAC names ✅

(c) Are named based on ring substituents only

(d) Are named as phenyl ketones

6. The common names of aldehydes are derived from:

(a) The parent hydrocarbon

(b) The corresponding alcohol

(c) The corresponding carboxylic acid ✅

(d) The corresponding ketone

7. A ketone is called symmetrical when:

(a) Both substituents are aromatic

(b) It contains only one alkyl group

(c) Both alkyl groups attached to the carbonyl carbon are identical ✅

(d) It contains substituents at alpha-positions

8. In common nomenclature of ketones, the alkyl groups are written:

(a) In the order of increasing molecular mass

(b) Randomly

(c) Alphabetically followed by the word “ketone” ✅

(d) According to IUPAC priority rules

9. The carbonyl carbon in aldehydes and ketones is:

(a) sp hybridized

(b) sp2 hybridized ✅

(c) sp3 hybridized

(d) Unhybridized

10. The aldehyde group (−CHO) is present in:

(a) Camphor only

(b) Most sugars and essential oils ✅

(c) All organic acids

(d) Only saturated hydrocarbons

11. Primary alcohols on oxidation produce:

(a) Ketones

(b) Aldehydes ✅

(c) Carboxylic acids

(d) Esters

12. Secondary alcohols on oxidation give:

(a) Aldehydes

(b) Acids

(c) Ketones ✅

(d) Esters

13. Ketones can also be prepared by:

(a) Dehydration of alkenes

(b) Hydration of alkynes ✅

(c) Polymerization

(d) Dehydrohalogenation

14. In the laboratory, formaldehyde is prepared by oxidation of:

(a) Ethyl alcohol

(b) Acetone

(c) Methyl alcohol (methanol) ✅

(d) Propanol

15. In the laboratory preparation of formaldehyde, the catalyst used is:

(a) Nickel

(b) Platinised asbestos or copper or silver ✅

(c) Palladium

(d) Iron

16. Formalin contains approximately:

(a) 20% formaldehyde

(b) 40% formaldehyde ✅

(c) 60% formaldehyde

(d) 80% formaldehyde

17. In the laboratory preparation of acetaldehyde, the oxidizing agent used is:

(a) Potassium permanganate

(b) Acidified sodium dichromate ✅

(c) Hydrogen peroxide

(d) Nitric acid

18. Industrial preparation of acetaldehyde uses ethylene and which catalyst?

(a) Nickel

(b) Iron oxide

(c) Palladium chloride with cupric chloride promoter ✅

(d) Cobalt catalyst

19. Acetone is commonly prepared by:

(a) Hydration of alkynes

(b) Dry distillation of calcium acetate ✅

(c) Oxidation of primary alcohols

(d) Oxidation of methane

20. The carbonyl group is reactive because it is:

(a) Non-polar

(b) Symmetrical

(c) Polar due to electronegativity difference between C and O ✅

(d) Negatively charged

21. The characteristic reaction of carbonyl compounds is:

(a) Electrophilic substitution

(b) Free radical substitution

(c) Nucleophilic addition reaction ✅

(d) Condensation reaction

22. In base-catalysed nucleophilic addition, the base:

(a) Acts as oxidizing agent

(b) Generates the nucleophile from reagent ✅

(c) Removes water

(d) Acts as reducing agent

23. The nucleophilic attack in the carbonyl group occurs on:

(a) Oxygen atom

(b) Hydrogen atom

(c) π-bond electrons

(d) Electrophilic carbon atom of carbonyl group ✅

24. Hydrogen cyanide (HCN) has low nucleophilicity because it:

(a) Is unstable

(b) Has no lone pair

(c) Does not ionize significantly to give CN^- ion ✅

(d) Is highly acidic

25. A suitable source of cyanide ion for cyanohydrin formation is:

(a) $NaHCO_3$

(b) NH_4Cl

(c) NaCN or KCN with HCl ✅

(d) CaO

26. Cyanohydrins on acidic hydrolysis give:

(a) Ethers

(b) Aldehydes

(c) Acetals

(d) α-Hydroxy carboxylic acids ✅

27. Grignard reagents react with aldehydes/ketones to form:

(a) Esters

(b) Carboxylic acids

(c) Alkanes

(d) Alcohols (after acidic hydrolysis) ✅

28. Sodium bisulphite reacts readily with:

(a) All ketones

(b) Aldehydes and small methyl ketones only ✅

(c) Aromatic amines

(d) Phenols

29. Bisulphite addition product is mainly used for:

(a) Dehydration

(b) Ester formation

(c) Purification and separation of aldehydes/ketones from alcohols ✅

(d) Neutralization

30. Sodium bisulphite ion acts as a nucleophile through:

(a) Oxygen atom

(b) Hydrogen atom

(c) Sulphur atom (more nucleophilic than oxygen) ✅

(d) Carbon atom

31. Condensation reactions involve:

(a) Breaking bonds

(b) Combination of two molecules with or without elimination of small molecules (H_2O/NH_3) ✅

(c) Halogenation

(d) Polymerization

32. Aldol condensation occurs in aldehydes/ketones which have:

(a) No α-hydrogen

(b) Aromatic rings

(c) At least one α-hydrogen atom present ✅

(d) Halo groups

33. Aldol contains which functional groups?

(a) Acid + Alcohol

(b) Ketone + Ether

(c) Aldehyde + Alcohol group in the same molecule ✅

(d) Amine + Alcohol

34. Heating an aldol with dilute acid gives:

(a) Alcohol

(b) α,β-Unsaturated carbonyl compound + water (dehydration) ✅

(c) Ketone only

(d) Ether

35. In aldol reaction, the carbanion is generated by:

(a) UV light

(b) Acid catalyst

(c) Removal of α-hydrogen by OH^- ion (base) ✅

(d) Oxidizing agent

36. Aldehydes without α-hydrogen undergo:

(a) Aldol condensation

(b) Polymerization

(c) Esterification

(d) Cannizzaro's reaction ✅

37. Cannizzaro's reaction gives:

(a) Two alcohols

(b) Two acids

(c) One alcohol + one salt of carboxylic acid (from same aldehyde) ✅

(d) Alkene + acid

38. Cannizzaro reaction is a:

(a) Substitution

(b) Self oxidation–reduction (disproportionation) reaction ✅

(c) Dehydration

(d) Cracking

39. The reagent required for Cannizzaro's reaction is:

(a) Dilute H_2SO_4

(b) H_2/Pd

(c) Conc. or 50% NaOH solution (strong base) ✅

(d) $KMnO_4$

40. Haloform reaction is given by:

(a) Aromatic aldehydes

(b) Aromatic ketones

(c) Acetaldehyde and methyl ketones (CH_3–CO–R) only ✅

(d) Long-chain ketones

41. The iodoform test is used to detect:

(a) All ketones

(b) Aromatic aldehydes

(c) Methyl ketones and ethanol ✅

(d) Methanol only

42. The iodoform test produces:

(a) White solid

(b) Red precipitate

(c) Yellow water-insoluble solid (CHI_3) ✅

(d) Silver mirror

43. Acid-catalysed nucleophilic addition is favoured by:

(a) Strong nucleophile

(b) Weak nucleophile ✅

(c) No nucleophile

(d) Neutral reagents

44. Acid catalysis in carbonyl compounds increases:

(a) Nucleophilic character of oxygen

(b) Basicity of carbon

(c) Electrophilic character of carbonyl carbon ✅

(d) Strength of π-bond

45. Formaldehyde polymerizes in the presence of dilute H_2SO_4 to form:

(a) Paraldehyde

(b) Metaformaldehyde ✅

(c) Ethanol

(d) Acetaldehyde

46. Aldehydes/ketones react with hydroxylamine to form:

(a) Hydrazones

(b) Phenylhydrazones

(c) Oximes ✅

(d) Acetals

47. Reaction of aldehydes/ketones with phenylhydrazine gives:

(a) Oximes

(b) Phenylhydrazones ✅

(c) Hydrazones

(d) Acetals

48. 2,4-Dinitrophenylhydrazine is used to:

(a) Reduce ketones

(b) Oxidize aldehydes

(c) Identify aldehydes and ketones ✅

(d) Form acetals

49. Aldehydes react with alcohols in presence of dry HCl to form:

(a) Ketones

(b) Aldols

(c) Acetals ✅

(d) Hydrazones

50. Aldehydes reduced with sodium borohydride give:

(a) Secondary alcohols

(b) Ketones

(c) Primary alcohols ✅

(d) Esters

51. Ketones reduced with sodium borohydride give:

(a) Primary alcohols

(b) Secondary alcohols ✅

(c) Tertiary alcohols

(d) Aldehydes

52. Sodium borohydride reduces:

(a) C=C bonds

(b) Aromatic rings

(c) Carbonyl group only ✅

(d) Carboxylic acids

53. Catalytic reduction of aldehydes with H_2 and Pd/Pt/Ni gives:

(a) Secondary alcohols

(b) Ketones

(c) Primary alcohols ✅

(d) Esters

54. Mild oxidizing agents like Tollen's reagent can oxidize:

(a) Ketones

(b) Aldehydes ✅

(c) Alkanes

(d) Alcohols only

55. Aldehydes oxidized by strong oxidizing agents give:

(a) Ketones

(b) Alcohols

(c) Carboxylic acids ✅

(d) Aldols

56. Ketones are resistant to oxidation by mild oxidizing agents because:

(a) C-H bond is weak

(b) They are volatile

(c) Strong C-C bond requires strong oxidants ✅

(d) They are basic

57. In unsymmetrical ketone oxidation, the carbon adjacent to the smaller number of hydrogen atoms is:

(a) Protected

(b) Preferentially oxidized ✅

(c) Converted to alcohol

(d) Converted to ketone

58. 2,4-DNPH test gives:

(a) White crystalline solid

(b) Red solution

(c) Yellow or orange crystalline precipitate ✅

(d) Silver mirror

59. Tollen's test is also called:

(a) Benedict's test

(b) Fehling's test

(c) Silver mirror test ✅

(d) Iodoform test

60. Fehling's solution test gives a brick-red precipitate with:

(a) All ketones

(b) Aromatic ketones

(c) Aliphatic aldehydes ✅

(d) Methanol

🩸 Keypoints Important Short Questions:

1. What is the functional group present in aldehydes and ketones?

Answer:

👉 Aldehydes and ketones contain the carbonyl group (C=O) as the functional group.

2. How are aldehydes prepared?

Answer:

👉 Aldehydes are prepared by the oxidation of primary alcohols.

3. How are ketones prepared?

Answer:

👉 Ketones are prepared by the oxidation of secondary alcohols.

4. What type of reactions do aldehydes and ketones undergo?

Answer:

👉 Both aldehydes and ketones undergo nucleophilic addition reactions, where the negative part of the reagent attacks the carbonyl carbon and the positive part goes to the oxygen atom.

5. What is aldol condensation?

Answer:

👉 Aldol condensation is the reaction in which two molecules of the same aldehyde or ketone containing α-hydrogen condense in the presence of dilute NaOH to form an aldol.

6. Which aldehydes undergo Cannizzaro's reaction?

Answer:

👉 Aldehydes without α-hydrogen atoms undergo Cannizzaro's reaction in the presence of concentrated NaOH, giving one molecule of alcohol and one molecule of carboxylic acid salt.

7. What is the haloform reaction?

Answer:

👉 Acetaldehyde and methyl ketones react with halogens in the presence of NaOH to give a haloform (CHX_3) and a carboxylic acid containing one carbon less than the parent compound.

8. How do aldehydes and ketones react with ammonia derivatives?

Answer:

👉 They react with $G–NH_2$ derivatives in the presence of acid to form condensation products containing C=N–G and water.

9. What is the reduction of aldehydes and ketones?

Answer:

👉 Aldehydes are reduced to primary alcohols and ketones to secondary alcohols using $NaBH_4$ or H_2 with Pd, Pt, or Ni catalyst.

10. Name two tests to distinguish aldehydes from ketones.

Answer:

👉 1. Tollen's reagent (Silver mirror test): Positive for aldehydes.

👉 2. Fehling's solution: Gives brick-red precipitate with aldehydes; ketones do not react.

🩸 Important Short Questions:

1. What are carbonyl compounds?

Answer:

👉 Organic compounds containing the carbonyl functional group (C=O) are called carbonyl compounds.

2. How do aldehydes differ from ketones in structure?

Answer:

👉 **In aldehydes**, the carbonyl group is bonded to at least one hydrogen and occurs at the end of a chain.

👉 **In ketones**, the carbonyl group is bonded to two carbon atoms and occurs within the chain.

3. Give the general formula of aldehydes and ketones.

Answer:

👉 The general formula of both aldehydes and ketones is C$_{\square}$H$_{2\square}$O.

4. Name two naturally occurring compounds containing aldehyde and ketone groups.

Answer:

👉 **Aldehyde group:** present in most sugars and essential oils.

👉 **Ketone group:** present in camphor and menthone.

5. How are the IUPAC names of ketones derived?

Answer:

👉 IUPAC names of ketones are derived from the corresponding alkane name by replacing the ending -e with -one. The position of the carbonyl group is indicated by numbering the chain from the nearest end.

6. How are aldehydes and ketones generally prepared?

Answer:

👉 **Aldehydes** are prepared by the oxidation of primary alcohols.

👉 **Ketones** are prepared by the oxidation of secondary alcohols or by hydration of alkynes.

7. Describe the laboratory preparation of formaldehyde.

Answer:

👉 **Formaldehyde** is prepared by passing a mixture of methyl alcohol vapours and air over a platinised asbestos, copper, or silver catalyst at 300°C.

👉 **The gaseous** formaldehyde is absorbed in water to give formalin (40% formaldehyde, 8% methyl alcohol, 52% water).

8. How is acetaldehyde prepared in the laboratory?

Answer:

👉 **Ethyl alcohol** is oxidised using acidified sodium dichromate solution.

👉 The **acetaldehyde** formed is immediately distilled off to prevent further oxidation to acetic acid.

9. How is acetone prepared industrially?

Answer:

👉 **Acetone** is prepared by the dry distillation of calcium acetate, producing acetone and calcium carbonate.

10. Explain why the carbonyl group is reactive.

Answer:

👉 **The carbonyl group** has a polar C=O bond with partial positive charge on carbon (electrophilic) and partial negative charge on oxygen (nucleophilic).

👉 **Most reactions** are nucleophilic addition reactions, catalysed by acids or bases, where the negative part of the reagent attacks the carbonyl carbon.

11. What is a base-catalysed nucleophilic addition reaction?

Answer:

👉 It is a reaction where a strong nucleophile attacks the electrophilic carbon of a carbonyl group in the presence of a base, forming an addition product.

12. How does hydrogen cyanide react with aldehydes and ketones?

Answer:

👉 **Hydrogen** cyanide adds to aldehydes and ketones to form cyanohydrins.

👉 **NaCN/HCl** is used to generate HCN in situ for the reaction.

13. What is the use of cyanohydrin formation?

Answer:

👉 Cyanohydrins are used to synthesize α-hydroxy acids, which have one more carbon atom than the starting aldehyde or ketone.

14. How do Grignard reagents react with aldehydes and ketones?

Answer:

👉 Grignard reagents add to aldehydes and ketones to form adducts, which on acidic hydrolysis give alcohols.

15. What is the reaction of aldehydes and small methyl ketones with sodium bisulphite?

Answer:

👉 They form a crystalline white precipitate called the sodium bisulphite addition product, used for separation and purification of carbonyl compounds.

16. Define condensation reactions.

Answer:

👉 Reactions in which two molecules combine to form a new compound with or without elimination of a small molecule like H_2O or NH_3 are called condensation reactions.

17. What is aldol condensation?

Answer:

👉 Aldehydes or ketones with α-hydrogen atoms react with dilute alkali to form aldols (β-hydroxy aldehydes or ketones), which dehydrate to form α,β-unsaturated carbonyl compounds.

18. Explain the mechanism of aldol formation.

Answer:

1. **Hydroxide** ion removes an α-hydrogen to form a carbanion.

2. **Carbanion** attacks the carbonyl carbon of another molecule.

3. **Alkoxide** ion is protonated to form the aldol.

19. What is Cannizzaro's reaction?

Answer:

👉 Aldehydes without α-hydrogen atoms undergo disproportionation in concentrated NaOH, producing one molecule of alcohol and one molecule of carboxylate salt.

20. Describe the mechanism of Cannizzaro's reaction.

Answer:

1. **Hydroxide ion** attacks the carbonyl carbon to form a complex anion.

2. **Hydride ions are** transferred to another molecule of aldehyde.

3. **Alcohol** and **carboxylate** salt are formed.

21. What is the haloform reaction?

Answer:

👉 Acetaldehyde and methyl ketones react with halogens in NaOH to give a haloform (CHX_3) and sodium salt of carboxylic acid.

22. Give the synthetic importance of the haloform reaction.

Answer:

👉 It converts a methyl ketone into a carboxylic acid with one carbon atom less than the parent compound.

23. What is iodoform test used for?

Answer:

👉 It is used to distinguish methyl ketones from other ketones, forming yellow CHI_3 precipitate.

24. Write the reaction of acetaldehyde with iodine and NaOH.

Answer:

👉 $CH_3CHO + 3I_2 + 4NaOH \longrightarrow CHI_3$ (yellow ppt) + HCOONa + 3NaI + $3H_2O$

25. Why are base-catalysed nucleophilic additions important?

Answer:

👉 They allow formation of alcohols, cyanohydrins, bisulphite addition products, and other derivatives, which are useful in synthesis and purification of carbonyl compounds.

26. What is the lodoform test?

Answer:

👉 The **lodoform** test is a haloform reaction using iodine and NaOH, forming yellow insoluble CHI_3.

👉 It **distinguishes** methyl ketones from other ketones, ethanol from methanol, and acetaldehyde from other aldehydes.

27. What happens in acid-catalysed nucleophilic addition reactions?

Answer:

👉 The carbonyl oxygen is protonated, increasing the electrophilic character of carbon, allowing weak nucleophiles to attack easily.

28. What products are formed when aldehydes react with ammonia derivatives?

Answer:

👉 Aldehydes react with ammonia derivatives (NH_2OH, NH_2NH_2, etc.) to form condensation products containing the C=N–G group and water.

29. How are oximes formed?

Answer:

👉 Aldehydes or ketones react with hydroxylamine (NH_2OH) in acid to form oximes.

30. How are hydrazones formed?

Answer:

👉 Aldehydes or ketones react with hydrazine (NH_2NH_2) in acid to form hydrazones.

31. What is the use of 2,4-DNPH test?

Answer:

👉 Aldehydes and ketones react with 2,4-dinitrophenylhydrazine to form yellow/orange crystalline solids, used for identification.

32. How are acetals formed?

Answer:

👉 Aldehydes react with alcohols in dry HCl to form acetals, protecting the aldehyde group from alkaline oxidation.

33. How can aldehydes and ketones be reduced?

Answer:

👉 Aldehydes ⟶ primary alcohols and ketones ⟶ secondary alcohols using:

- $NaBH_4$ (hydride source)
- H_2 with Pd, Pt, or Ni (catalytic reduction)

34. Why are aldehydes easily oxidised?

Answer:

👉 Aldehydes have a hydrogen atom attached to the carbonyl carbon, which can be oxidised to form carboxylic acids.

35. How are ketones oxidised?

Answer:

👉 **Ketones** resist mild oxidising agents and are oxidised only by strong agents ($K_2Cr_2O_7/H_2SO_4$, $KMnO_4/H_2SO_4$).

👉 **Oxidation** attacks carbon atoms adjacent to carbonyl.

36. What is the 2,4-DNPH test used for?

Answer:

👉 It is used to detect aldehydes and ketones, forming yellow or orange crystalline precipitates.

37. Describe Tollen's (Silver Mirror) test.

Answer:

👉 **Aldehydes** react with ammoniacal silver nitrate on warming to form a silver mirror.

👉 **Ketones** do not react.

38. Describe Fehling's and Benedict's test.

Answer:

👉 **Aliphatic aldehydes** react with Fehling's or Benedict's solution on boiling to give a brick-red precipitate of Cu_2O.

👉 **Ketones** do not react.

39. What is the sodium nitroprusside test?

Answer:

👉 **Ketones** produce a wine-red or orange-red colour with alkaline sodium nitroprusside.

👉 **Aldehydes** do not react.

40. List some uses of formaldehyde and acetaldehyde.

Answer:

👉 **Formaldehyde:** Resins (urea-formaldehyde), plastics (bakelite), disinfectant, silvering mirrors, vaccine processing.

👉 **Acetaldehyde:** Production of acetic acid, n-butanol, ethyl acetate, rubber accelerators, hypnotic drugs (chloral hydrate), antiseptic inhalant.

🩸 EXERCISE

Q1. Fill in the blanks:

(i) Aldehydes are the first oxidation product of _____.

Answer: primary alcohols ✅

(ii) Ketones are the first oxidation product of _____.

Answer: secondary alcohols ✅

(iii) Aldehydes and ketones undergo _____ addition reactions.

Answer: nucleophilic ✅

(iv) Formaldehyde reacts with _____ to give primary alcohol.

Answer: $NaBH_4$ ✅

(v) Acetaldehyde reacts with _____ to give 2-butanol.

Answer: Grignard reagent ✅

(vi) Aldehydes are strong _____ agents.

Answer: reducing ✅

(vii) The oxidation of an _____ always gives a carboxylic acid.

Answer: aldehyde ✅

(viii) The reduction of a _____ always gives a secondary alcohol.

Answer: ketone ✅

(ix) Formaldehyde gives _____ test with Tollen's reagent.

Answer: silver mirror ✅

(x) Acetaldehyde gives a _____ precipitate with Fehling's solution.

Answer: brick-red ✅

Q2. Indicate True or False:

(i) Formaldehyde is used in the silvering of mirrors.

Answer: True ✅

(ii) Ketones combine with alcohols in the presence of HCl gas to form acetals.

Answer: False ❌

(iii) Acetaldehyde undergoes Cannizzaro's reaction.

Answer: False ❌

(iv) Aldol condensation reaction is given by only those aldehydes and ketones which contain an α-hydrogen atom.

Answer: True ✅

(v) Cannizzaro's reaction is given by only those aldehydes containing no α-hydrogen atom.

Answer: True ✅

(vi) Propanal and propanone behave differently with Tollen's reagent.

Answer: True ✅

(vii) Acetone reacts with sodium bisulphite to give a yellow crystalline product.

Answer: False ❌ (It gives a white crystalline adduct)

(viii) Acetone on reduction gives a primary alcohol.

Answer: False ❌ (It gives a secondary alcohol)

(ix) 40% aqueous solution of formaldehyde is called formalin.

Answer: True ✅

Q.3 Multiple Choice Questions — Encircle the correct answer.

(i) The carbon atom of a carbonyl group is

(a) sp hybridized

(b) sp^2 hybridized ✅

(c) sp^3 hybridized

(d) none of these

(ii) Formalin is

(a) 10% solution of formaldehyde in water

(b) 20% solution of formaldehyde in water

(c) 40% solution of formaldehyde in water ✅

(d) 60% solution of formaldehyde in water

(iii) Which of the following will have the highest boiling point?

(a) Methanal

(b) Ethanal

(c) Propanal

(d) 2-Hexanone ✅

(iv) Ketones are prepared by the oxidation of

(a) Primary alcohol

(b) Secondary alcohol ✅

(c) Tertiary alcohol

(d) all of these

(v) Acetone reacts with HCN to form a cyanohydrin. It is an example of

(a) Electrophilic addition

(b) Electrophilic substitution

(c) Nucleophilic addition ✅

(d) Nucleophilic substitution

(vi) Which of the following compounds will not give iodoform test on treatment with I_2/NaOH:

(a) Acetaldehyde

(b) Acetone

(c) Butanone

(d) 3-Pentanone ✅

(vii) Which of the following compounds will react with Tollen's reagent.

(a) $CH_3–CHO$ ✅

(b) $CH_3–CO–CH_3$

(c) $CH_3–CH_2–OH$

(d) $CH_3–CO–CH_2–CH_3$

(viii) Cannizzaro's reaction is not given by

(a) Formaldehyde

(b) Acetaldehyde ✅

(c) Benzaldehyde

(d) Trimethylacetaldehyde

(ix) Which of the following reagents will react with both aldehydes and ketones?

(a) Grignard reagent ✅

(b) Tollen's reagent

(c) Fehling's reagent

(d) Benedict's reagent

🌟 **Q.4 Give one laboratory and one industrial method for the preparation of formaldehyde.**

❖ **Introduction:**

Formaldehyde (HCHO) is the simplest aldehyde and is commonly used as formalin (a 40% aqueous solution). It is prepared from methanol oxidation, both in the laboratory and on an industrial scale.

🔬 1. Laboratory Method of Preparation of Formaldehyde

👉 Principle

In the laboratory, formaldehyde is prepared by oxidizing methanol vapours in the presence of a metallic catalyst at high temperature.

👉 Reaction

$$2\ CH_3OH + O_2 \longrightarrow (\text{Pt-asbestos, } 300\ ^\circ C)\ 2\ HCHO + 2\ H_2O$$

👉 Procedure (Step-by-Step)

1. Vapours of methyl alcohol (methanol) are produced by gentle heating.

2. Air is passed through methanol using a suction pump.

3. The mixture of air + methanol vapours is passed over a platinised asbestos / copper / silver catalyst heated to 300°C.

4. Methanol gets oxidised to formaldehyde gas.

5. This gas is passed into cold water, where it dissolves to form formalin.

👉 Resulting Product (Formalin Composition)

- 40% formaldehyde
- 8% methanol
- 52% water

🏭 2. Industrial Method of Preparation of Formaldehyde

👉 Principle

Industrially, methanol is oxidised in the presence of metal oxide catalysts at higher temperature to obtain large quantities of formaldehyde.

👉 Reaction

$2\ CH_3OH + O_2 \longrightarrow (Fe_2O_3 - MoO_3 \text{ or Ag, } 500\ ^\circ C)\ 2\ HCHO + 2\ H_2O$

👉 Procedure

1. A mixture of methanol vapours + air is fed into a large oxidation reactor.

2. The mixture passes over iron oxide–molybdenum oxide (Fe_2O_3–MoO_3) catalyst

OR silver catalyst, maintained at 500°C.

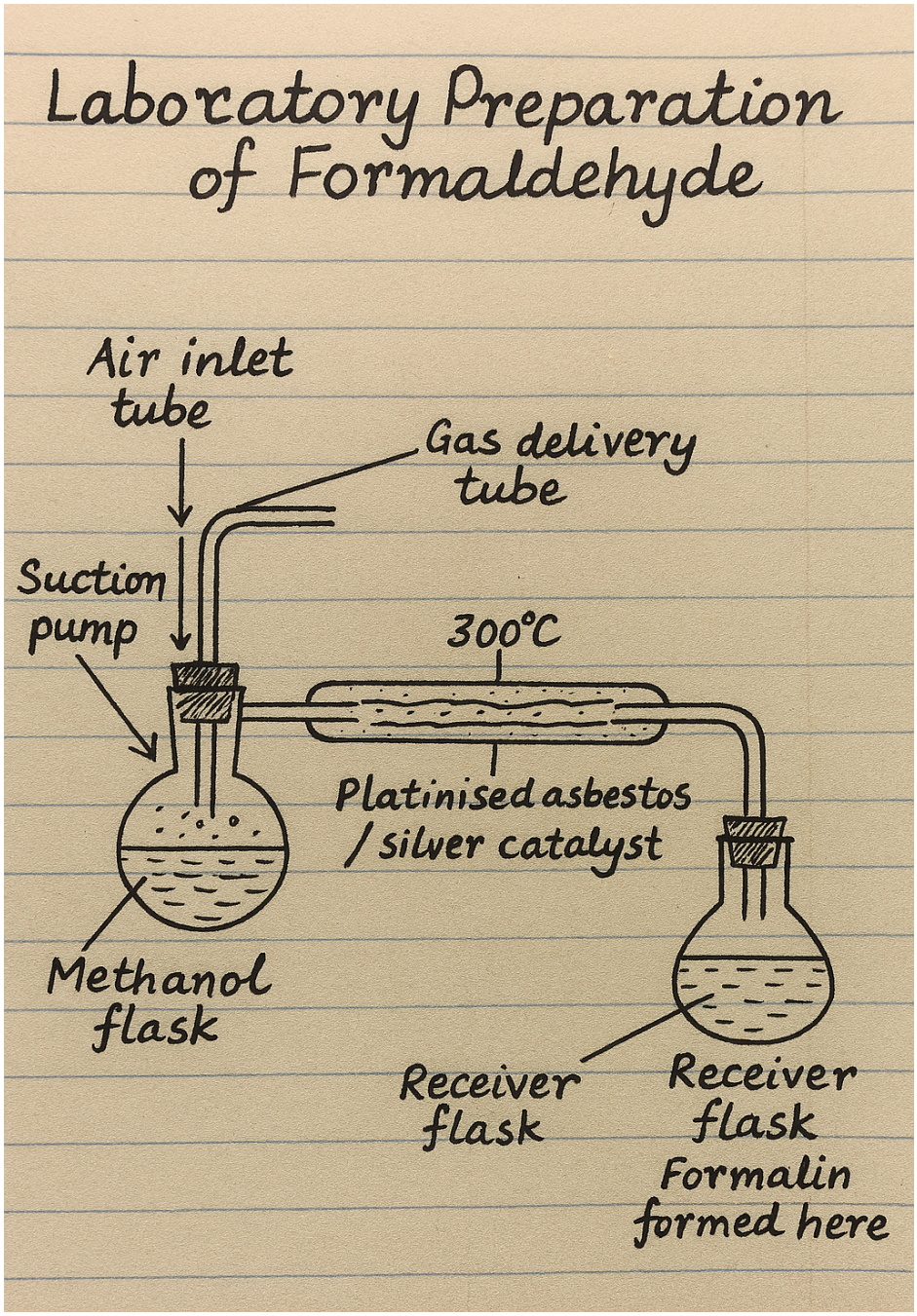
3. Oxidation occurs and formaldehyde gas is formed.

4. The product gases are cooled and absorbed in water to produce formalin.

👉 Why industrial method is efficient?

- Less time
- Continuous production
- High yield
- Economical at large scale

✦ **Digram:**



✦ **Summary:**

- Formaldehyde is prepared by oxidising methanol.

- **Laboratory Method:** Methanol vapours + air ⟶ passed over platinised asbestos at 300°C.
- **Industrial Method:** Methanol + air ⟶ passed over Fe_2O_3–MoO_3 or Ag catalyst at 500°C.
- **The final product** is formalin (40% formaldehyde solution).

🌟 **Q.5 How does formaldehyde react with the following reagents?**

i) Reaction with CH_3MgI (Grignard Reagent)

Reaction Type: Nucleophilic addition

$$HCHO + CH_3MgI \longrightarrow CH_3CH_2OMgI$$

$$CH_3CH_2OMgI + H_2O \longrightarrow CH_3CH_2OH + Mg(OH)I$$

Product: Primary alcohol (Ethanol)

👉 Formaldehyde always gives primary alcohols with Grignard reagents.

ii) Reaction with HCN (Hydrogen Cyanide)

Reaction Type: Nucleophilic addition

$HCHO + HCN \longrightarrow HO{-}CH_2{-}CN$

Product: Formaldehyde cyanohydrin

👉 CN^- attacks carbonyl carbon → gives cyanohydrin.

iii) Reaction with $NaHSO_3$ (Sodium bisulphite)

Reaction Type: Bisulphite addition

$HCHO + NaHSO_3 \longrightarrow HO{-}CH_2{-}SO_3Na$

Product: White crystalline bisulphite addition compound

👉 All aldehydes form stable crystalline sodium bisulphite compounds.

iv) Reaction with conc. NaOH (Cannizzaro Reaction)

Formaldehyde has no α-hydrogen → gives Cannizzaro reaction.

Reaction:

$2\ HCHO + NaOH \longrightarrow HCOONa + CH_3OH$

Products:

- Sodium formate (oxidation product)
- Methanol (reduction product)

👉 One molecule is oxidised, the other reduced.

v) Reaction with $NaBH_4$ / H_2O

Reaction Type: Reduction

$HCHO \longrightarrow (NaBH_4 / H_2O)\ CH_3OH$

Product: Methanol (primary alcohol)

👉 $NaBH_4$ reduces aldehydes to alcohols.

vi) Reaction with Tollen's Reagent

Reaction Type: Oxidation

$HCHO + 2[Ag(NH_3)_2]^+ + H_2O \longrightarrow HCOOH + 2Ag + 4NH_3$

Product:

- Silver mirror on test tube
- Formic acid formed

👉 Formaldehyde gives positive Tollen's test.

vii) Reaction with Fehling's Reagent

Reaction:

$HCHO + 2Cu^{2+} + 5OH^- \longrightarrow HCOO^- + Cu_2O$ (red ppt) $+ 3H_2O$

Product:

- Brick-red precipitate of Cu_2O
- Formate ion

👉 Formaldehyde reduces Fehling's solution strongly.

✦ Summary (Super Easy for Revision)

Reagent	Product
CH_3MgI	Ethanol
HCN	Cyanohydrin
$NaHSO_3$	Bisulphite compound
Conc. NaOH	Sodium formate + methanol (Cannizzaro)
$NaBH_4/H_2O$	Methanol
Tollen's	Silver mirror
Fehling's	Brick-red precipitate

🌟 Q.6 Give one laboratory and one industrial method for the preparation of acetaldehyde.

⭐ Laboratory Method for Preparation of Acetaldehyde

1. Oxidation of Ethyl Alcohol (Ethanol)

This is the most common laboratory preparation.

Reagents:

- Acidified sodium dichromate ($Na_2Cr_2O_7 + H_2SO_4$)

Reaction:

$CH_3CH_2OH + [O] \longrightarrow CH_3CHO + H_2O$

Process:

- A mixture of ethanol and sodium dichromate is added slowly into boiling dilute sulphuric acid.
- A vigorous reaction occurs.
- Acetaldehyde distils off immediately, preventing further oxidation to acetic acid.
- On redistillation, pure acetaldehyde is obtained.

Key Point:

👉 Ethanol (a primary alcohol) gives acetaldehyde on oxidation.

⭐ Industrial Method for Preparation of Acetaldehyde

2. Oxidation of Ethylene (Wacker Process)

This is the modern industrial method.

Catalyst:

- **Palladium** chloride ($PdCl_2$)
- **Copper(II)** chloride ($CuCl_2$) as promoter

Reaction:

$CH_2=CH_2 + O_2 \longrightarrow (PdCl_2, CuCl_2)\ 2\ CH_3CHO$

Process:

- **Ethylene** gas is oxidised by air in the presence of $PdCl_2$ catalyst.
- **Pd^{2+}** converts ethylene to acetaldehyde.
- **$CuCl_2$** regenerates **Pd^{2+}** from Pd^0, allowing continuous reaction.

Industrial Importance:

👉 This process gives high yield of acetaldehyde at low cost.

✦ **Summary:**

Laboratory Method:

- Oxidation of ethanol using acidified sodium dichromate.

Industrial Method:

- Air oxidation of ethylene using $PdCl_2$ / $CuCl_2$ (Wacker process).

🌟 Q.7 How does acetaldehyde react with the following reagents?

(i) C_2H_5MgI (Ethylmagnesium iodide – Grignard reagent)

Reaction:

Acetaldehyde reacts with C_2H_5MgI to form an addition product, which on hydrolysis gives a secondary alcohol (2-butanol).

$CH_3CHO + C_2H_5MgI \longrightarrow CH_3CH(OMgI)C_2H_5$

Hydrolysis: $CH_3CH(OH)C_2H_5 + Mg(OH)I$

✔ **Product**: 2-Butanol

(ii) HCN

Acetaldehyde forms a cyanohydrin.

$CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN \longrightarrow CH_3CH(OH)CN$

✔ **Product:** Acetaldehyde cyanohydrin

(iii) $NaHSO_3$ (Sodium bisulphite)

Forms a bisulphite addition product (white crystalline solid).

$CH_3CHO + NaHSO_3 \longrightarrow CH_3CH(OH)SO_3Na$

✔ Used for purification of aldehydes.

(iv) Dilute NaOH (Aldol condensation)

Acetaldehyde undergoes aldol condensation because it contains α-hydrogen.

$2\ CH_3CHO \rightarrow[\text{dil. NaOH}]\ CH_3CH(OH)CH_2CHO$

✔ **Product:** 3-Hydroxybutanal (Aldol)

(v) I_2 / NaOH (Iodoform test)

Acetaldehyde gives a positive iodoform test.

$$CH_3CHO + 3\ I_2 + 4\ NaOH \longrightarrow CHI_3 + HCOONa + 3\ NaI + 3\ H_2O$$

✔ **Product:** Yellow precipitate of iodoform (CHI_3)

(vi) $NaBH_4$ / H_2O (Reduction)

$NaBH_4$ reduces acetaldehyde to primary alcohol (ethanol).

$$CH_3CHO + NaBH_4 \longrightarrow CH_3CH_2OH$$

✔ **Product**: Ethanol

(vii) NH_2OH (Hydroxylamine)

Acetaldehyde reacts with hydroxylamine to form an oxime.

$CH_3CHO + NH_2OH \longrightarrow CH_3CH{=}NOH + H_2O$

✔ **Product:** Acetaldehyde oxime

(viii) $K_2Cr_2O_7$ / H_2SO_4 (Oxidation)

Strong oxidizing agents convert acetaldehyde to acetic acid.

$CH_3CHO + [O] \longrightarrow CH_3COOH$

✔ **Product**: Acetic acid

✦ Summary Table (Quick Revision)

Reagent	Product
C_2H_5MgI	2-Butanol
HCN	Cyanohydrin
$NaHSO_3$	Bisulphite adduct
Dil. NaOH	Aldol (3-Hydroxybutanal)
I_2/NaOH	Iodoform (CHI_3)
$NaBH_4/H_2O$	Ethanol
NH_2OH	Oxime
$K_2Cr_2O_7/H_2SO_4$	Acetic acid

🌟 Q.8 Describe briefly the mechanism of nucleophilic addition to a carbonyl compound

✦ Introduction:

The carbonyl group (C=O) in aldehydes and ketones is polar due to the difference in electronegativity between carbon and oxygen.

- Oxygen is partially negative (δ^-) ⟶ nucleophilic character
- Carbon is partially positive (δ^+) ⟶ electrophilic character

This polarity allows nucleophiles (electron-rich species) to attack the carbon atom of the carbonyl group.

General Mechanism

Step 1: Nucleophilic attack on carbonyl carbon

$R_2C{=}O + Nu^- \longrightarrow R_2C(NU)O^-$

- The **nucleophile** (Nu^-) attacks the electrophilic carbon.
- The **π-electrons** of C=O move to oxygen, forming an alkoxide ion.

Step 2: Protonation of oxygen

$R_2C(NU)O^- + H^+ \longrightarrow R_2C(NU)OH$

- The negatively charged oxygen picks up a proton from water or acid.
- This gives the final addition product (alcohol derivative).

Acid vs. Base Catalysis

Type	Role
Acid-catalysed	Protonation of carbonyl oxygen ↑ electrophilic character of carbon ⟶ easier nucleophilic attack.
Base-catalysed	Generates stronger nucleophile (Nu^-) ⟶ attacks carbonyl carbon.

Note: The final product is the same in both cases; only the mechanism differs slightly.

Example: Addition of HCN to Acetaldehyde

$CH_3CHO + HCN \longrightarrow^{(NaCN/HCl)} CH_3CH(OH)CN$

- Cyanide ion attacks carbonyl carbon ⟶ alkoxide intermediate.
- Protonation of oxygen ⟶ cyanohydrin.

✦ **Summary:**

1. Carbonyl carbon is electrophilic; oxygen is nucleophilic.

2. Nucleophile attacks carbon → alkoxide intermediate forms.

3. Protonation of oxygen → final addition product.

4. Reaction can be acid- or base-catalysed, depending on the nucleophile.

🌟 **Q.9 Explain with mechanism the addition of ethylmagnesium bromide to acetaldehyde. What is the importance of this reaction?**

❖ **Introduction:**

The reaction of Grignard reagents (RMgX) with aldehydes and ketones is a nucleophilic addition reaction.

- **Ethylmagnesium** bromide (C_2H_5MgBr) acts as a nucleophile, attacking the electrophilic carbon of the carbonyl group.

- **Aldehydes** produce secondary alcohols, whereas ketones produce tertiary alcohols.

Reaction type: Nucleophilic addition to carbonyl compounds.

Reaction with Acetaldehyde

$CH_3CHO + C_2H_5MgBr \rightarrow (ether)\ CH_3CH(OC_2H_5MgBr)$

Hydrolysis: $CH_3CH(OH)C_2H_5 + Mg(OH)Br$

- This is an intermediate alkoxide.
- Hydrolysis with dilute acid (H_3O^+) gives the final alcohol:

$CH_3CH(OC_2H_5MgBr) + H_2O \rightarrow CH_3CH(OH)C_2H_5 + Mg(OH)Br$

Overall Reaction:

$CH_3CHO + C_2H_5MgBr + H_2O \rightarrow CH_3CH(OH)C_2H_5$

Product: 2-butanol (a secondary alcohol)

Mechanism

Step 1: Nucleophilic attack

- The ethyl group ($C_2H_5^-$) from Grignard attacks the electrophilic carbonyl carbon.
- The C=O π-bond shifts electrons to oxygen → forming an alkoxide ion.

```
O                                   O^-

||          C2H5^-                  |

CH3 - C - H  ----------> CH3 - C - C2H5

                                    |

                                   MgBr^+
```

Step 2: Protonation

Alkoxide is protonated by water or dilute acid → secondary alcohol forms.

```
CH3 - C - C2H5  +  H2O  --> CH3 - C - C2H5
```

| |

O^- OH

- **Final product:** $CH_3CH(OH)C_2H_5$

Importance of the Reaction

1. Synthesis of Alcohols

- Converts aldehydes and ketones to primary, secondary, or tertiary alcohols depending on the carbonyl compound.

2. Carbon-Carbon Bond Formation

- Grignard reagents extend carbon chains, useful in organic synthesis.

3. Versatility

- **Can react** with formaldehyde $\longrightarrow$ primary alcohol
- **Acetaldehyde** $\longrightarrow$ secondary alcohol

- **Ketones** ⟶ tertiary alcohol

4. Key Step in Organic Synthesis

- Used in pharmaceuticals, fragrances, and fine chemicals.

✦ **Summary:**

- **Grignard** reagent is a strong nucleophile.
- **Acetaldehyde** reacts ⟶ intermediate alkoxide ⟶ hydrolysis ⟶ 2-butanol.
- **Reaction** is important for alcohol synthesis and carbon-carbon bond formation.

🌟 **Q.10 Explain with mechanism the addition of sodium bisulphite to acetone. What is the utility of this reaction?**

❖ **Introduction:**

- **Sodium bisulphite** ($NaHSO_3$) reacts with aldehydes and some ketones to form water-soluble crystalline addition products.
- The **reaction** is nucleophilic addition at the carbonyl carbon.

- The **product** can be used for purification and separation of carbonyl compounds.
- **Reaction type:** Base-catalysed nucleophilic addition.

Reaction with Acetone

$CH_3COCH_3 + NaHSO_3 \longrightarrow CH_3C(OH)SO_3NaCH_3$

Product: Sodium bisulphite addition product (white crystalline solid)

Mechanism

Step 1: Ionization of Sodium Bisulphite

$NaHSO_3 \rightleftharpoons Na^+ + HSO_3^-$

- HSO_3^- acts as a nucleophile.

Step 2: Nucleophilic Attack on Carbonyl Carbon

- The **nucleophilic** sulphite ion attacks the electrophilic carbon of the carbonyl group.

- The **C=O π-bond** shifts electrons to oxygen, forming an alkoxide intermediate.

O O^-

|| HSO3^- |

CH3 - C - CH3 ----------> CH3 - C - CH3

|

SO3^-

Step 3: Protonation

Alkoxide gets protonated by water ⟶ formation of stable bisulphite addition product.

CH3 - C - CH3 + H+ --> CH3 - C(OH)-CH3-SO3Na

| |

O^- OH

The product is a white crystalline solid, soluble in water, insoluble in ether.

Utility of the Reaction

1. Purification of Carbonyl Compounds

- Aldehydes and small ketones form crystalline bisulphite adducts ⟶ can be separated from non-carbonyl impurities.

2. Identification of Aldehydes/Ketones

- Formation of white crystalline solid confirms the presence of a carbonyl group.

3. Regeneration of Parent Carbonyl Compound

- On treatment with dilute acid, the bisulphite adduct regenerates the original aldehyde or ketone.

$$CH_3C(OH)SO_3NaCH_3 + HCl \longrightarrow CH_3COCH_3 + NaHSO_3 + H_2O$$

4. Analytical and Synthetic Use

- Useful in analysis and storage of aldehydes/ketones in pure form.

✦ **Summary:**

Sodium bisulphite adds to the electrophilic carbon of the carbonyl group in acetone.

Forms a stable, water-soluble adduct.

Useful for purification, identification, and storage of carbonyl compounds.

🌟 **Q.11 Describe with mechanism aldol condensation reaction. Why formaldehyde does not give this reaction?**

❖ **Introduction:**

- Aldol condensation is a base-catalysed reaction in which aldehydes or ketones containing at least one α-hydrogen react with cold dilute alkali to form β-hydroxy aldehydes

(aldols) or β-hydroxy ketones, which on heating dehydrate to form α,β-unsaturated carbonyl compounds.

- The name “aldol” comes from the presence of both aldehyde (–CHO) and alcohol (–OH) functional groups in the product.
- **Reaction type:** Nucleophilic addition and subsequent condensation.

Reaction Example (Aldehyde: Ethanal)

$2\ CH_3CHO \xrightarrow{(dil.NaOH)} CH_3CH(OH)CH_2CHO$

- **Product:** 3-Hydroxybutanal (aldol)
- **On heating:**

$CH_3CH(OH)CH_2CHO \xrightarrow{(\Delta)} CH_3CH{=}CHCHO + H_2O$

- Product after dehydration: Crotonaldehyde

Mechanism of Aldol Condensation

Step 1: Formation of Enolate Ion

- The **hydroxide** ion (OH^-) abstracts an α-hydrogen from aldehyde/ketone.
- **This forms** a resonance-stabilized carbanion (enolate ion).

$CH_3CH_2CHO + OH^- \longrightarrow CH_3CH^-CHO + H_2O$

Resonance:

$CH_3CH^-CHO \Leftrightarrow CH_3C=CH-O^-$

Step 2: Nucleophilic Attack on Carbonyl Carbon

- The enolate ion acts as a nucleophile and attacks the electrophilic carbonyl carbon of another aldehyde molecule.
- Forms an alkoxide intermediate.

CH3CH^-CHO + CH3CHO ---> CH3CH(OH)CH2CHO

- Protonation of alkoxide by water gives β-hydroxy aldehyde (aldol).

Step 3: Dehydration (On Heating)

- **On heating** or in presence of dilute acid/base, aldol loses water.
- **Forms α,β**-unsaturated aldehyde with a C=C bond.

$CH_3CH(OH)CH_2CHO \longrightarrow CH_3CH=CHCHO + H_2O$

Why Formaldehyde Does Not Give Aldol Condensation

1. Aldol condensation requires α-hydrogen (hydrogen on the carbon adjacent to the carbonyl group).

2. Formaldehyde (H–CHO) has no α-hydrogen, since the carbonyl carbon is directly attached to hydrogen atoms only.

3. Therefore, no enolate ion can form, and no aldol product is obtained.

✦ **Summary:**

- **Aldol condensation:** Two molecules of aldehyde/ketone with α-hydrogen react under dilute base to give

β-hydroxy aldehyde/ketone, which dehydrates to α,β-unsaturated carbonyl compound.

- **Formaldehyde** does not undergo aldol condensation due to the absence of α-hydrogen.

🌟 **Q.12 What types of aldehydes give Cannizzaro's reaction? Give its mechanism.**

❖ **Introduction:**

Cannizzaro's reaction is a disproportionation reaction in which two molecules of an aldehyde react in the presence of concentrated alkali to give:

- One molecule reduced to alcohol
- One molecule oxidized to carboxylic acid (as its salt)

$$2\ R{-}CHO \xrightarrow{conc.NaOH} R{-}CH_2OH + R{-}COONa$$

- **Reaction type:** Self oxidation-reduction (disproportionation)

Important:

- **Only aldehydes** without **α-hydrogen** undergo Cannizzaro's reaction.
- **Aldehydes with** α-hydrogen (like acetaldehyde) undergo aldol condensation instead.

Example: Benzaldehyde

$$2\ C_6H_5CHO + NaOH \longrightarrow C_6H_5CH_2OH + C_6H_5COONa$$

✦ Mechanism of Cannizzaro's Reaction

Step 1: Nucleophilic Attack by Hydroxide Ion

- The hydroxide ion (OH^-) attacks the electrophilic carbonyl carbon of the aldehyde to form a tetrahedral alkoxide intermediate.

$$C_6H_5{-}CHO + OH^- \longrightarrow [C_6H_5{-}C(OH)_2]^-$$

Step 2: Hydride Transfer

- The **alkoxide** ion transfers a hydride ion (H^-) to another aldehyde molecule.

- **One aldehyde** gets reduced to alcohol, the other gets oxidized to carboxylate ion.

$[C_6H_5–C(OH)_2]^- + C_6H_5–CHO \longrightarrow C_6H_5–CH_2OH + C_6H_5–COO^-$

Step 3: Formation of Products

- The carboxylate ion reacts with Na^+ from the base to form sodium salt of the acid.

$C_6H_5–COO^- + Na^+ \longrightarrow C_6H_5COONa$

The other aldehyde molecule is reduced to benzyl alcohol.

✦ **Summary:**

- Cannizzaro reaction occurs only with aldehydes lacking α-hydrogen.
- **Products:** One molecule of alcohol and one molecule of carboxylate salt.
- **Reaction type:** Disproportionation (simultaneous oxidation & reduction).

Example: Benzaldehyde, formaldehyde

🌟 Q.13 Explain the mechanism of the reaction of phenylhydrazine with acetone

❖ Introduction:

- **Phenylhydrazine** ($C_6H_5NHNH_2$) reacts with aldehydes or ketones to form phenylhydrazones.
- **This reaction** is a condensation reaction (addition followed by elimination of water).
- It is acid-catalyzed.

Example: Reaction with acetone

$$CH_3–CO–CH_3 + C_6H_5NH–NH_2 \xrightarrow{(H^+)} CH_3–C=N–NH–C_6H_5 + H_2O$$

Mechanism of Phenylhydrazone Formation

Step 1: Protonation of Carbonyl Oxygen

- In acidic medium, the carbonyl oxygen is protonated to make the carbonyl carbon more electrophilic.

$$CH_3–C(OH^+)–CH_3$$

Step 2: Nucleophilic Attack by Phenylhydrazine

- The nitrogen of phenylhydrazine attacks the electrophilic carbonyl carbon.
- A tetrahedral intermediate (carbinolamine) is formed.

$$CH_3–C(OH)–CH_3 + H_2N–NH–C_6H_5 \longrightarrow CH_3–C(OH)–NH–NH–C_6H_5$$

Step 3: Proton Transfer

- A proton is transferred from nitrogen to oxygen to facilitate water elimination.

Step 4: Elimination of Water

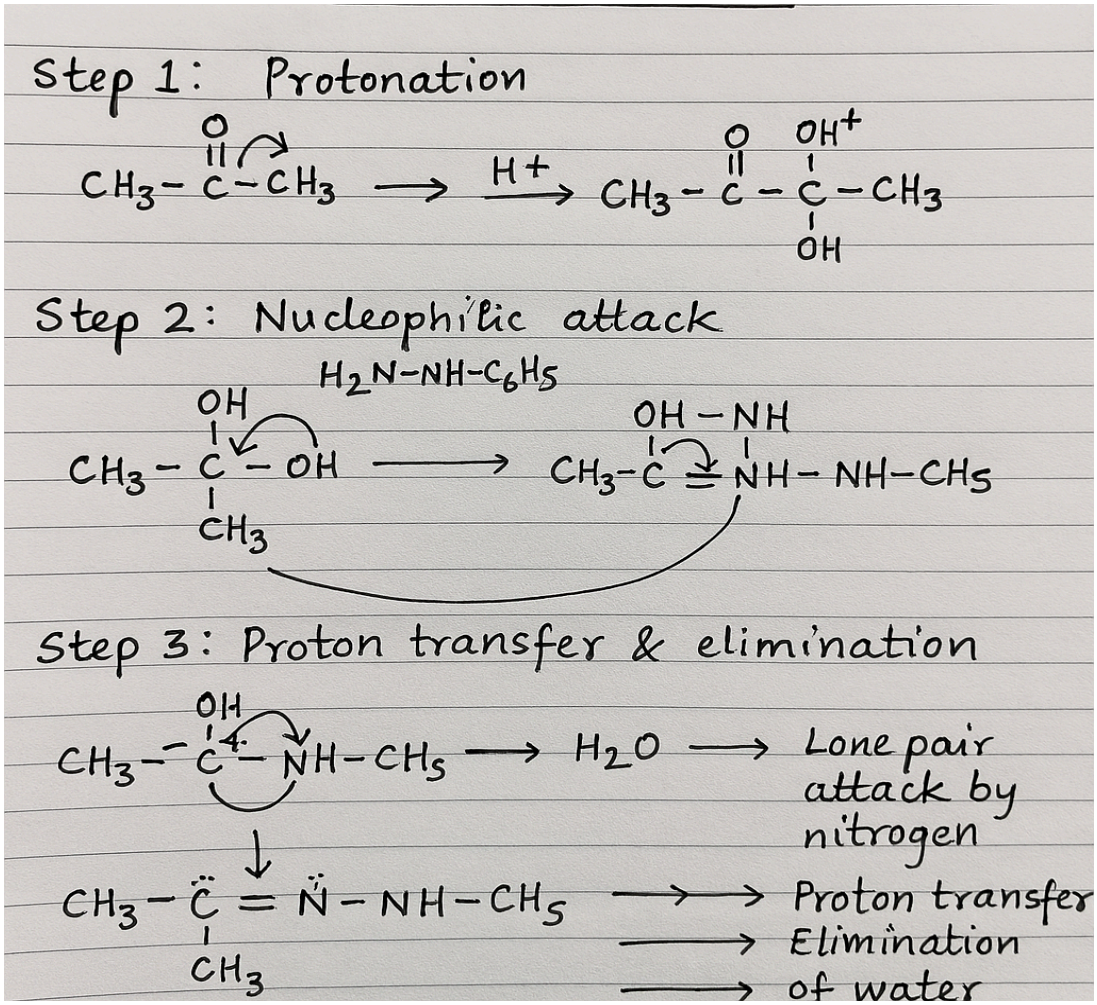
- Water is eliminated from the intermediate to form a C=N double bond (imino group).

$$CH_3–C(OH)–NH–NH–C_6H_5 \longrightarrow CH_3–C=N–NH–C_6H_5 + H_2O$$

Step 5: Formation of Phenylhydrazone

- The **final product** is acetone phenylhydrazone, a yellow or orange crystalline solid.
- **Reaction** is used for identification of ketones and aldehydes.

✦ **Digram:**



✦ **Summary:**

- **Reagents:** Acetone + Phenylhydrazine (acidic medium)

- **Reaction type:** Condensation (addition-elimination)
- **Product:** Phenylhydrazone + Water
- **Utility:** Identification of ketones/aldehydes (qualitative test)

🌟 **Q.14 Using ethyne as a starting material, how would you get acetaldehyde, acetone, and ethyl alcohol?**

❖ **Introduction:**

- **Ethyne** (C_2H_2) can serve as a starting material for synthesizing various carbonyl compounds and alcohols.
- The **conversions** mainly involve hydration, oxidation, or hydrogenation reactions.

1️⃣ Preparation of Acetaldehyde (CH_3CHO)

Reaction: Hydration of ethyne in the presence of $HgSO_4$ / H_2SO_4

$$C_2H_2 + H_2O \longrightarrow (HgSO_4 / H_2SO_4)\ CH_3{-}CHO$$

Explanation:

- Water adds across the triple bond.

- The intermediate enol tautomerizes to form the aldehyde.
- This gives acetaldehyde.

Mechanism Concept:

1. Protonation of triple bond ⟶ formation of vinyl cation

2. Nucleophilic attack by water ⟶ enol

3. Tautomerization ⟶ aldehyde

2 Preparation of Acetone (CH_3COCH_3)

Reaction: Hydration of propyne ($CH_3C{\equiv}CH$) in the presence of $HgSO_4$ / H_2SO_4

$CH_3{-}C{\equiv}CH + H_2O \longrightarrow (HgSO_4 / H_2SO_4)\ CH_3{-}CO{-}CH_3$

Explanation:

- Hydration of an internal alkyne gives a ketone.
- Propyne ($CH_3C{\equiv}CH$) is an internal alkyne ⟶ forms acetone.

Mechanism Concept:

1. Electrophilic addition of H^+ to triple bond ⟶ stable carbocation

2. Nucleophilic attack by water ⟶ enol

3. Tautomerization ⟶ ketone

3 Preparation of Ethyl Alcohol (CH_3CH_2OH)

Step 1: Partial hydrogenation of ethyne to ethene

$C_2H_2 + H_2 \longrightarrow$(Lindlar catalyst) C_2H_4

Step 2: Acid-catalyzed hydration of ethene

$C_2H_4 + H_2O \longrightarrow (H_2SO_4)\ CH_3CH_2OH$

Explanation:

- **Ethyne is first** converted to ethene using a selective hydrogenation catalyst.

- **Ethene reacts** with water in the presence of H_2SO_4 to give ethanol.

✦ **Summary:**

Ethyne ⟶ Aldehyde, Ketone, Alcohol

1. Acetaldehyde: Ethyne + H_2O / $HgSO_4$ ⟶ enol ⟶ tautomerization ⟶ CH_3CHO

2. Acetone: Propyne + H_2O / $HgSO_4$ ⟶ enol ⟶ tautomerization ⟶ CH_3COCH_3

3. Ethyl alcohol: Ethyne ⟶ (H_2/Lindlar) ⟶ Ethene + H_2O / H_2SO_4 ⟶ CH_3CH_2OH

4. Concepts: Hydration ⟶ carbonyl; tautomerization ⟶ stable product; partial hydrogenation ⟶ alkene.

🌟 **Q. 15: Mechanism of Addition of HCN to Acetone**

Reaction:

$CH_3–CO–CH_3$ + HCN ⟶(NaCN/HCl) $CH_3–C(OH)–CH_3–CN$

Mechanism (Stepwise):

1. Generation of nucleophile:

HCN is weakly ionized. NaCN provides cyanide ions (CN^-), which act as nucleophiles.

$NaCN \longrightarrow Na^+ + CN^-$

2. Nucleophilic attack:

CN^- attacks the electrophilic carbon of the carbonyl group in acetone.

$CH_3–CO–CH_3 + CN^- \longrightarrow CH_3–C(CN)–O^–CH_3$

3. Protonation:

The alkoxide ion (O^-) abstracts a proton (H^+) from HCN or water to form the hydroxyl group.

$CH_3–C(CN)–O^- + H^+ \longrightarrow CH_3–C(OH)–CH_3–CN$

Product: Acetone cyanohydrin (contains both –OH and –CN groups)

Importance of Reaction:

1. Forms cyanohydrins, useful intermediates in the synthesis of α-hydroxy acids.

2. Adds one carbon atom to the original carbonyl compound.

3. Useful in organic synthesis for building larger molecules.

🌟 Q. 16: Detailed Explanation of Organic Conversions

Here's a step-by-step detailed explanation of how each transformation occurs, including the type of reaction and reagents used.

(i) Acetone ⟶ t-Butyl alcohol

- **Type of reaction:** Reduction of a ketone.
- **Reagent:** Strong reducing agent like $LiAlH_4$ or $NaBH_4$.

Mechanism:

- **The hydride** ion (H^-) attacks the electrophilic carbonyl carbon of acetone.
- **The carbonyl** oxygen is protonated to give a tertiary alcohol.

$(CH_3)_2CO + H^- \rightarrow (NaBH_4 / H_2O)\ (CH_3)_2CHOH$

(ii) Propanal ⟶ 1-Propanol

- **Type of reaction:** Reduction of aldehyde.
- **Reagents:** $NaBH_4$ or catalytic hydrogenation (H_2/Pd).

Mechanism:

- **Hydride** ions attack the carbonyl carbon of propanal.
- **After protonation**, the aldehyde is converted into a primary alcohol.

$CH_3CH_2CHO + H^- \rightarrow CH_3CH_2CH_2OH$

(iii) Propanone ⟶ 2-Propanol

Type of reaction: Reduction of ketone.

Reagents: $NaBH_4$ or H_2 with a catalyst.

Mechanism:

- **Hydride** ion attacks the carbonyl carbon of propanone.
- **Protonation** gives a secondary alcohol.

$CH_3COCH_3 + H^- \longrightarrow CH_3CHOHCH_3$

(iv) Methanal → Ethanal

Type of reaction: Carbon chain elongation via cyanohydrin formation.

Reagents: HCN → cyanohydrin → hydrolysis.

Mechanism:

- **HCN** adds to the carbonyl carbon of methanal to form a cyanohydrin.

- **Acidic hydrolysis** converts the nitrile (−CN) to an aldehyde.

$HOCH_2CN \xrightarrow{(H^+/H_2O)} CH_3CHO$

(v) Ethanal → Propanone

- **Type of reaction:** Aldol condensation followed by oxidation.
- **Reagents:** Dilute NaOH, then oxidizing agent.

Mechanism:

- Two **molecules** of ethanal undergo aldol condensation (α-hydrogen abstraction → nucleophilic attack).
- **The β**-hydroxy aldehyde formed is oxidized to a ketone.

$2CH_3CHO \xrightarrow{(dil.NaOH)} CH_3CH(OH)CH_2CHO$

(vi) Ethanal → 2-Propanol

- **Type of reaction:** Grignard addition.
- **Reagent:** CH_3MgBr followed by hydrolysis.

Mechanism:

- **Nucleophilic** attack of the Grignard reagent on carbonyl carbon.
- **Acidic hydrolysis** protonates the intermediate alkoxide to yield a secondary alcohol.

$CH_3CHO + CH_3MgBr \rightarrow (H^+/H_2O)\ CH_3CHOHCH_3$

(vii) Ethyne → Ethanal

- **Type of reaction:** Acid-catalyzed hydration.
- **Reagents:** $HgSO_4/H_2SO_4$.

Mechanism:

- The triple bond of ethyne reacts with water in the presence of Hg^{2+}.
- Forms enol → tautomerizes to aldehyde.

$HC \equiv CH + H_2O \rightarrow (HgSO_4 / H_2SO_4)\ CH_3CHO$

(viii) Ethene → Ethanal

- **Type of reaction:** Hydroformylation (oxo process).
- **Reagents:** CO + H_2 in presence of a metal catalyst (like Co or Rh).

Mechanism:

- Addition of CO and H_2 across the double bond of ethene to form ethanal.

$CH_2=CH_2 + CO + H_2 \longrightarrow CH_3CHO$

(ix) Ethanal ⟶ Ethanol

- **Type of reaction:** Reduction.
- **Reagents:** $NaBH_4$ or H_2/catalyst.

Mechanism:

- Hydride attacks carbonyl carbon ⟶ protonation ⟶ primary alcohol.

$CH_3CHO + H^- \longrightarrow CH_3CH_2OH$

(x) Ethanol ⟶ 2-Butanone

- **Type of reaction:** Carbon chain elongation via Grignard + oxidation.
- **Reagents:** CH_3MgBr, then oxidation with PCC/CrO_3.

Mechanism:

- Ethanol ⟶ reacts with CH_3MgBr to form secondary alcohol ⟶ oxidized to ketone.

$CH_3CH_2OH \longrightarrow (CH_3MgBr)\ CH_3CH(OH)CH_3 \longrightarrow ([O])\ CH_3COCH_3$

(xi) Methanol ⟶ Ethanal

- **Type of reaction:** Oxidation and carbon chain elongation.
- **Reagents:** PCC or $Cr_2O_7^{2-}/H_2SO_4$ for initial oxidation ⟶ HCN addition ⟶ hydrolysis.

Mechanism:

- Methanol oxidized to formaldehyde ⟶ cyanohydrin formation ⟶ hydrolysis ⟶ ethanal.

(xii) Ethanol ⟶ Ethanoic acid

- **Type of reaction**: Oxidation of primary alcohol.
- **Reagents:** $K_2Cr_2O_7/H_2SO_4$ or $KMnO_4$.

Mechanism:

- Alcohol oxidized to aldehyde (ethanal) ⟶ further oxidized to carboxylic acid (ethanoic acid).

$CH_3CH_2OH + [O] \longrightarrow CH_3CHO + [O] \longrightarrow CH_3COOH$

✦ **Summary:**

- **Aldehydes** can be reduced to primary alcohols; ketones to secondary alcohols.
- **Grignard** reagents can elongate carbon chains by forming alcohols.
- **Aldol** condensation allows formation of larger carbonyl compounds from aldehydes.
- **Oxidation** of aldehydes produces carboxylic acids; ketones resist mild oxidation.
- **Hydroformylation** and hydration of alkynes/alkenes can form aldehydes.

- **Chain elongation** is often achieved via cyanohydrin formation.

🌟 Q.17 Distinguishing Carbonyl Compounds

(i) Methanal (HCHO) and Ethanal (CH3CHO)

- **Tollen's Test:** Both give silver mirror ⟶ not useful.
- **Fehling's Test:** Both give brick-red ppt ⟶ not useful.
- **Iodoform Test:** Ethanal gives yellow iodoform ppt, methanal does not.
- Distinguishing reagent: Iodoform test.

(ii) Ethanal (CH3CHO) and Propanone (CH3COCH3)

- **Tollen's Test:** Ethanal ⟶ silver mirror, Propanone ⟶ no reaction.
- **Iodoform Test:** Both give yellow iodoform ppt.
- Distinguishing reagent: Tollen's test.

(iii) Ethanal (CH3CHO) and Propanal (CH3CH2CHO)

- **Iodoform Test:** Ethanal ⟶ yellow ppt, Propanal ⟶ no reaction.
- **Fehling's Test:** Both give brick-red ppt.

- Distinguishing reagent: Iodoform test.

(iv) Acetone (CH_3COCH_3) and Ethyl Alcohol (CH_3CH_2OH)

- **Iodoform Test:** Acetone ⟶ yellow ppt, Ethyl alcohol ⟶ yellow ppt.
- **Oxidation Test:** Acetone ⟶ no change with mild oxidizing agent, Ethyl alcohol ⟶ oxidized to ethanal.
- **Distinguishing reagent:** Oxidation test (or Tollen's test: acetone negative, ethanol positive after oxidation).

(v) Butanone ($CH_3CH_2COCH_3$) and 3-Pentanone ($CH_3CH_2COCH_2CH_3$)

- **Iodoform Test:** Butanone ⟶ positive (CH_3CO- group present), 3-Pentanone ⟶ negative.
- **Distinguishing reagent:** Iodoform test.

(vi) Acetaldehyde (CH_3CHO) and Benzaldehyde (C_6H_5CHO)

- **Fehling's Test:** Acetaldehyde ⟶ brick-red ppt, Benzaldehyde ⟶ no reaction. ✅
- **Tollen's Test:** Acetaldehyde ⟶ silver mirror, Benzaldehyde ⟶ silver mirror also positive.
- **Distinguishing reagent**: Fehling's solution.

(vii) 2-Pentanone ($CH_3CH_2COCH_2CH_3$) and 3-Pentanone ($CH_3CH_2CH_2COCH_3$)

- **Iodoform Test:** 2-Pentanone ⟶ positive (methyl ketone CH_3CO-), 3-Pentanone ⟶ negative.
- **Distinguishing reagent:** Iodoform test.

✦ **Summary:**

1. Iodoform Test: Detects CH_3CO- group ⟶ yellow ppt.

2. Tollen's Test: Aldehydes ⟶ silver mirror, Ketones ⟶ negative.

3. Fehling's/Benedict's Test: Aldehydes with α-hydrogen ⟶ brick-red ppt, Aromatic aldehydes ⟶ negative.

4. Oxidation Test: Primary alcohols/aldehydes ⟶ oxidized, Ketones/secondary alcohols ⟶ resist mild oxidizing agents.

🌟 Q.18 Oxidation of Aldehydes and Ketones

- **Aldehydes** and ketones show very different oxidation behavior.
- **Aldehydes** are easily oxidized, while ketones are resistant to oxidation.

(a) Oxidation of Aldehydes

- Aldehydes are readily oxidized because they contain the −CHO group, in which the carbonyl carbon is more easily attacked by an oxidizing agent.

General oxidation reaction

$R-CHO \rightarrow ([O])\ R-COOH$

(b) Oxidation of Ketones

👉 Ketones are difficult to oxidize because they lack a hydrogen atom on the carbonyl carbon.

👉 They generally do not react with mild oxidizing agents.

👉 They are oxidized only by strong oxidizing agents, and that too with breakage of C–C bonds, forming smaller carboxylic acids.

(i) Oxidation with $K_2Cr_2O_7$ / H_2SO_4

Aldehydes

Aldehydes are strongly oxidized by acidified potassium dichromate:

Reaction:

$$3R{-}CHO + K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow 3R{-}COOH + Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O$$

Color change:

- **Orange dichromate** ⟶ green chromium(III) sulfate.
- **This is an** important confirmatory test for aldehydes.

Ketones

Ketones do not react with $K_2Cr_2O_7$ under normal conditions.

Only very strong oxidation breaks carbon–carbon bonds:
Example (propanone):

$CH_3COCH_3 \rightarrow$(strong oxidation) $CH_3COOH + CO_2 + H_2O$

But in lab tests ⟶ no reaction.

(ii) Oxidation with Tollen's Reagent (Ammoniacal $AgNO_3$)

Aldehydes

- Aldehydes are easily oxidized to carboxylate ions.

Reaction:

$R–CHO + 2Ag^+ + 3OH^- \rightarrow R–COO^- + 2Ag(s) + 2H_2O$

Observation:

✔ Silver mirror forms inside the test tube.

This is an important qualitative test for aldehydes.

Ketones

Ketones do not react with Tollen's reagent.

Reason: They cannot be oxidized without breaking C–C bonds.

Observation: No silver mirror is formed.

(iii) Oxidation with Fehling's Solution

Aldehydes

Aldehydes containing α-hydrogen (aliphatic aldehydes) give positive results for Fehling's test.

Reaction:

$$R{-}CHO + 2Cu^{2+} + 5OH^{-} \longrightarrow R{-}COO^{-} + Cu_2O(s) + 3H_2O$$

Observation:

✔ Formation of brick-red precipitate of Cu_2O.

Ketones

- Ketones do not reduce Fehling's reagent.

Observation:

✘ No precipitate.

Exception:

α-hydroxy ketones may give positive test, but simple ketones like acetone, butanone do not.

✦ **Summary:**

Aldehydes

- Oxidized easily.
- With $K_2Cr_2O_7$ ⟶ carboxylic acids (orange ⟶ green).
- With Tollen's ⟶ silver mirror.
- With Fehling's ⟶ brick-red ppt.

Ketones

- Resistant to oxidation.
- No reaction with $K_2Cr_2O_7$ (under mild conditions).
- No reaction with Tollen's reagent.
- No reaction with Fehling's solution.
- Strong oxidation breaks C—C bonds.

🌟 Q.19 Reduction of Aldehydes and Ketones

Aldehydes and ketones undergo reduction to form alcohols.

The type of alcohol produced depends on whether the starting compound is an aldehyde or ketone:

- Aldehyde ⟶ Primary alcohol
- Ketone ⟶ Secondary alcohol

Two important reducing agents are:

1. Sodium borohydride ($NaBH_4$ / H_2O)

2. Hydro„zgen gas with pallsadium cy,dnatalsyst (H_2 / Pd),

(a) Reduction of Aldehydes

(i) Reduction with $NaBH_4$ / H_2O

$NaBH_4$ is a mild reducing agent that selectively reduces the C=O group.

General reaction:

$$R-CHO \longrightarrow (NaBH_4 / H_2O)\ R-CH_2OH$$

Example:

Ethanal $\longrightarrow$ Ethanol

CH_3CHO \xrightarrow[]{NaBH_4/H_2O} CH_3CH_2OH

Mechanism:

1. Hydride ion (H^-) from BH_4^- attacks carbonyl carbon.

2. Forms alkoxide ion.

3. Alkoxide is protonated by water → primary alcohol.

(ii) Reduction with H_2 / Pd (Catalytic Hydrogenation)

Aldehydes are hydrogenated to primary alcohols.

R−CHO + H_2 \xrightarrow[]{Pd} R−CH_2OH

Example:

Methanal ⟶ Methanol

HCHO + H_2 \xrightarrow[]{Pd} CH_3OH

(b) Reduction of Ketones

(i) Reduction with $NaBH_4$ / H_2O

Ketones are reduced to secondary alcohols.

General reaction:

R−CO−R' \xrightarrow[]{NaBH_4/H_2O} R−CHOH−R'

Example:

Propanone ⟶ 2-propanol

$$(CH_3)_2CO \xrightarrow[]{NaBH_4/H_2O} CH_3–CHOH–CH_3$$

Mechanism:

Same as aldehydes:

Hydride attack ⟶ alkoxide ⟶ protonation ⟶ secondary alcohol.

(ii) Reduction with H_2 / Pd

Catalytic hydrogenation also reduces ketones to secondary alcohols.

$$R–CO–R' + H_2 \xrightarrow[]{Pd} R–CH(OH)–R'$$

Example:

Butanone ⟶ 2-butanol

CH_3COCH_2CH_3 \xrightarrow[]{Pd}
CH_3–CH(OH)–CH_2CH_3

✦ **Summary:**

- Aldehydes ⟶ primary alcohols
- Ketones ⟶ secondary alcohols

$NaBH_4$ / H_2O

- Mild reducing agent
- Selective for C=O group
- Aldehyde ⟶ primary alcohol
- Ketone ⟶ secondary alcohol

H_2 / Pd

- Catalytic hydrogenation
- Converts both aldehydes and ketones into corresponding alcohols
- Faster and stronger than $NaBH_4$

🌟 Q.20 — Three uses of Formaldehyde and Acetaldehyde

👉 Uses of Formaldehyde (HCHO)

1. Manufacture of Bakelite plastic — used in electrical goods and adhesives.

2. As a preservative — used in laboratories and in embalming fluids.

3. Disinfectant — used for sterilizing surgical instruments and rooms.

👉 Uses of Acetaldehyde (CH_3CHO)

1. Manufacture of acetic acid — major industrial use.

2. Production of pyridine derivatives, perfumes, and dyes.

3. As a solvent in various organic reactions and in the rubber industry.

Note:

This chapter is designed to provide a solid foundation of knowledge, with the goal of deepening understanding and

encouraging further exploration of the subject. The content has been carefully selected to support effective learning and inspire students to engage with the topic more deeply.

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Purpose: To contribute to education by offering insightful, valuable content that enhances learning and understanding.

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