



CHAPTER # 8

CARBOYNL

COMPOUNDS

I: ALDEHYDES

AND KETONES

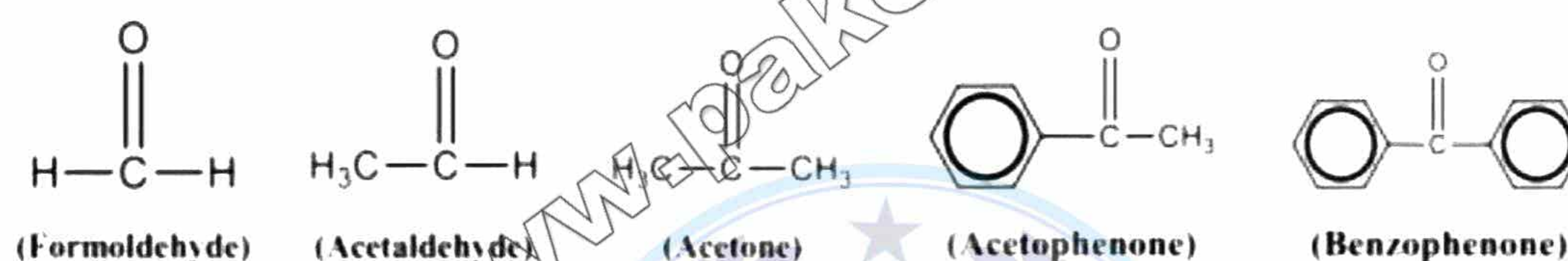
INTRODUCTION

Aldehydes and ketones hold significant importance, with widespread usage in several industries. They are the simplest carbonyl compounds; both contain a carbonyl group, which is a functional group consisting of a carbon atom double-bonded to an oxygen atom.

Aldehyde contain a carbonyl group at the terminal carbon of their carbon chain, whereas ketone have a carbonyl group located on the carbon within their carbon chain.

Both types of compounds have unique properties and reactivity due to the presence of the carbonyl group, which makes them useful in a variety of applications.

The typical representatives of this class of compounds are formaldehyde, acetone, benzaldehyde and acetophenone. Formaldehyde is exceptional since it carries two hydrogen atoms instead of alkyl substituents.



Organic chemistry emphasizes the study of aldehyde and ketones due to their significant applications in various industrial sectors.

For example, formaldehyde is used to produce resins, synthetic plastic and urea formaldehyde. Acetone is used in the preparation of iodoform, chloroform and nail polish remover. Benzaldehyde is used in the manufacturing of dyes etc.

PHYSICAL PROPERTIES

Physical State:

Methanal and ethanal are gases; the other lower aldehydes and ketones are colourless liquids at room temperature. The higher aldehydes and ketones (more than C_{20}) are solids at room temperature.

Odour:

Lower aldehydes have a pungent smell whereas ketones and higher aldehydes have a pleasant smell.

Boiling Point:

Carbonyl compounds have higher boiling points than alkanes of similar molecular weights due to the polar nature of the carbonyl group, enabling intermolecular forces.

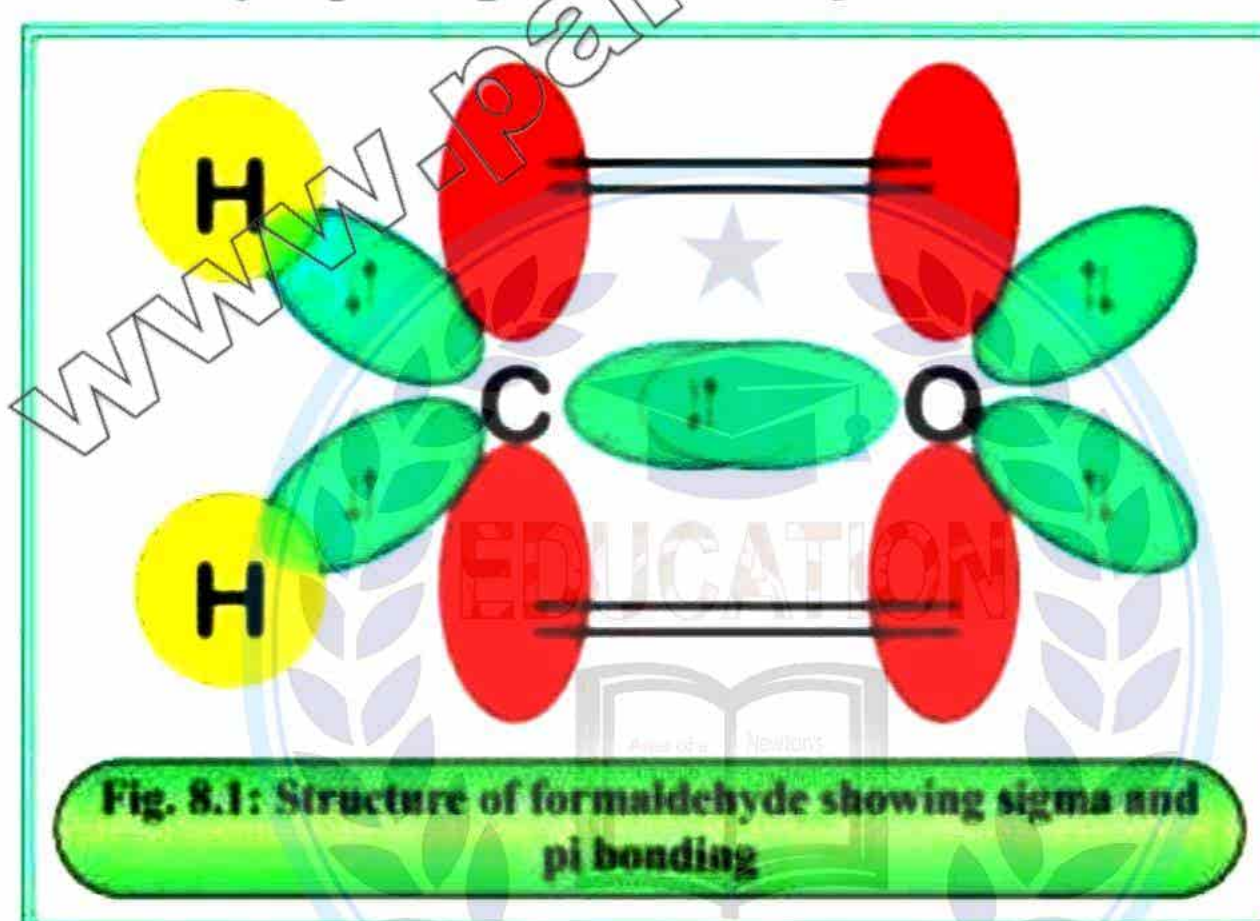
However, they have lower boiling points compared to alcohols and carboxylic acids due to the absence of intermolecular hydrogen bonding.

Solubility:

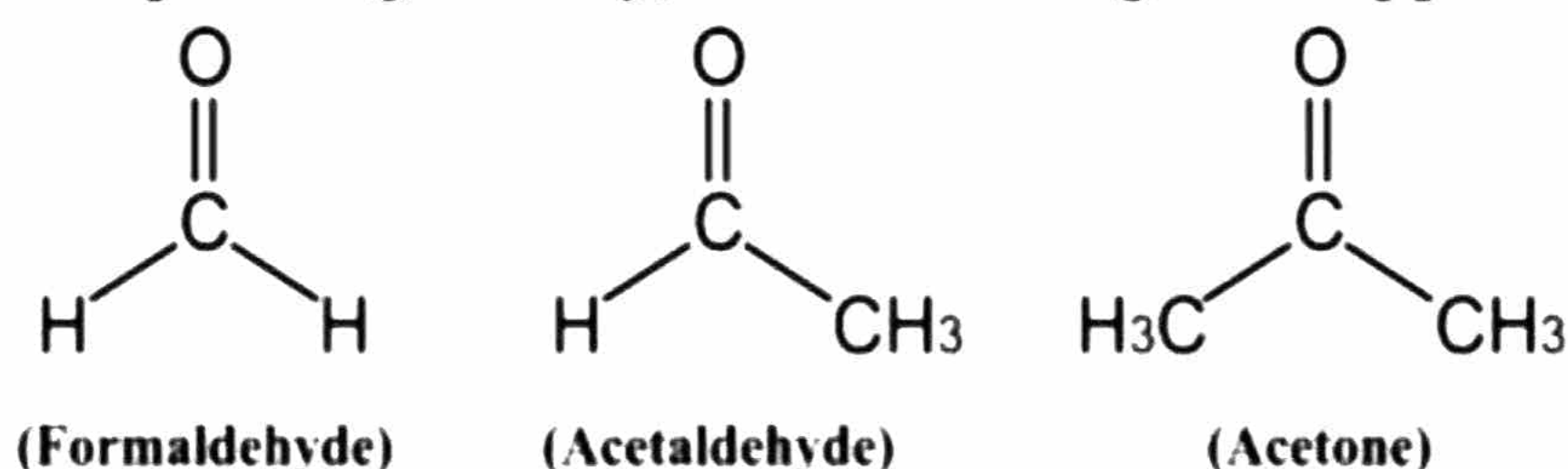
Carbonyl compounds are generally polar, and they are soluble in polar solvents such as water and ethanol. However, their solubility decreases as the size of the hydrophobic group (hydrocarbon chain) attached to the carbonyl carbon increases.

STRUCTURE OF ALDEHYDES AND KETONES

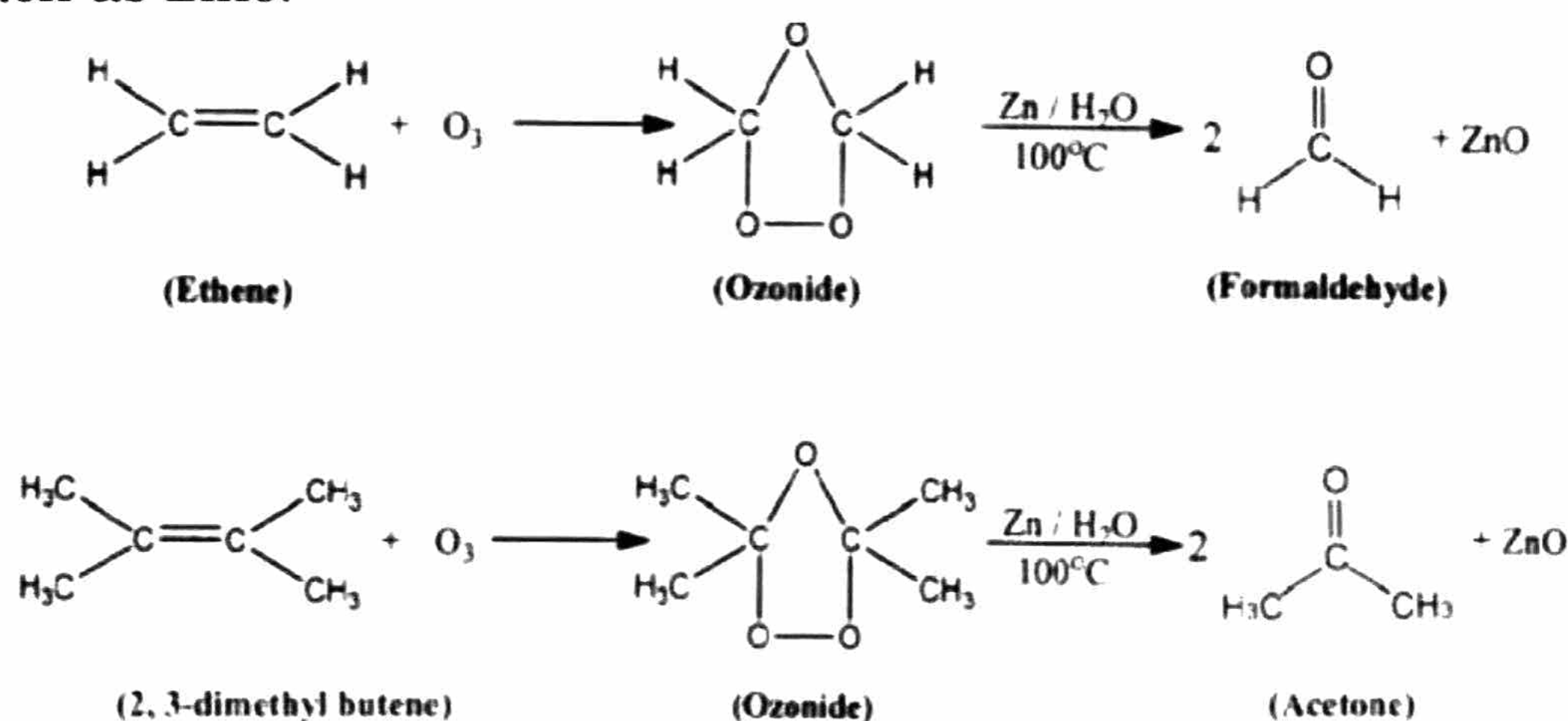
In aldehyde and ketone, the carbonyl group comprises a carbon atom that is double bonded to an oxygen atom. The carbon atom in the carbonyl group is sp^2 hybridized, with one of its sp^2 hybrid orbitals participating in sigma bond formation with the oxygen atom, while the other two sp^2 hybrid orbitals form sigma bonds with other atoms. The un hybrid p orbital of the carbon atom in the carbonyl group forms a pi bond with the Oxygen atom.



The sp^2 hybridization of the carbon atom in the carbonyl group allows it to acquire a trigonal planar geometry, with bond angles of approximately 120° .

**PREPARATION OF ALDEHYDES AND KETONES****Ozonolysis of Alkenes**

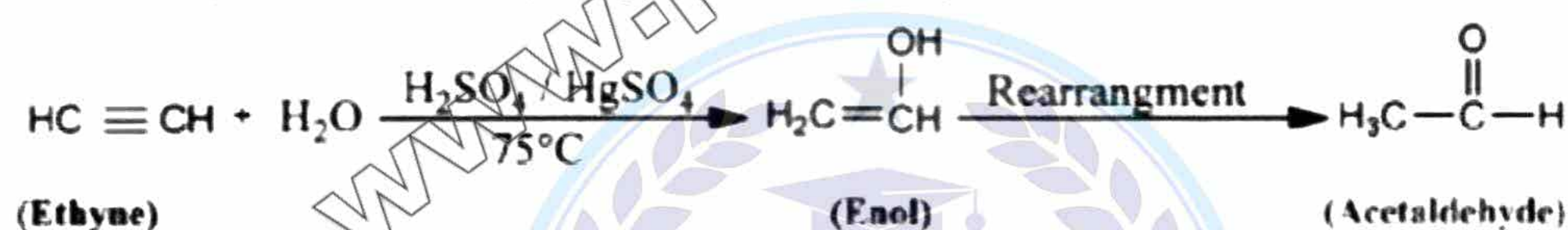
Alkenes can be ozonolyzed to yield aldehydes and ketones. This reaction involves the breaking of C-C of alkene by the use of ozone and reducing agent such as Zinc.



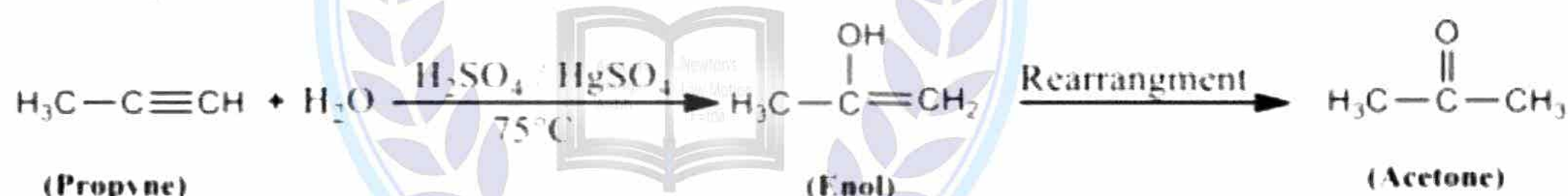
Hydration of Alkyne

Alkynes when heated with water in the presence of H_2SO_4 and HgSO_4 , an acid catalyzed addition reaction occur on $\text{C}\equiv\text{C}$ to form an unstable enol which then on tautomerization, gives aldehyde or Ketone.

(i) The hydration of ethyne gives acetaldehyde

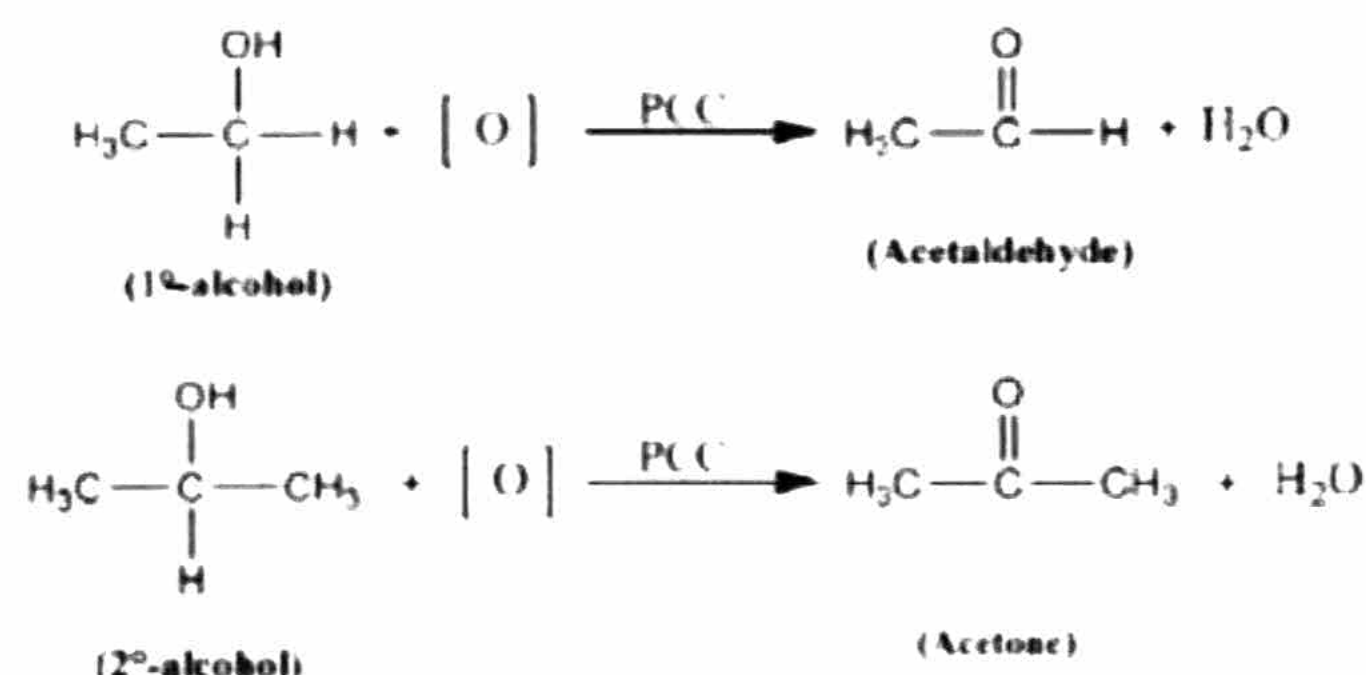


(ii) The hydration of propyne gives propanone



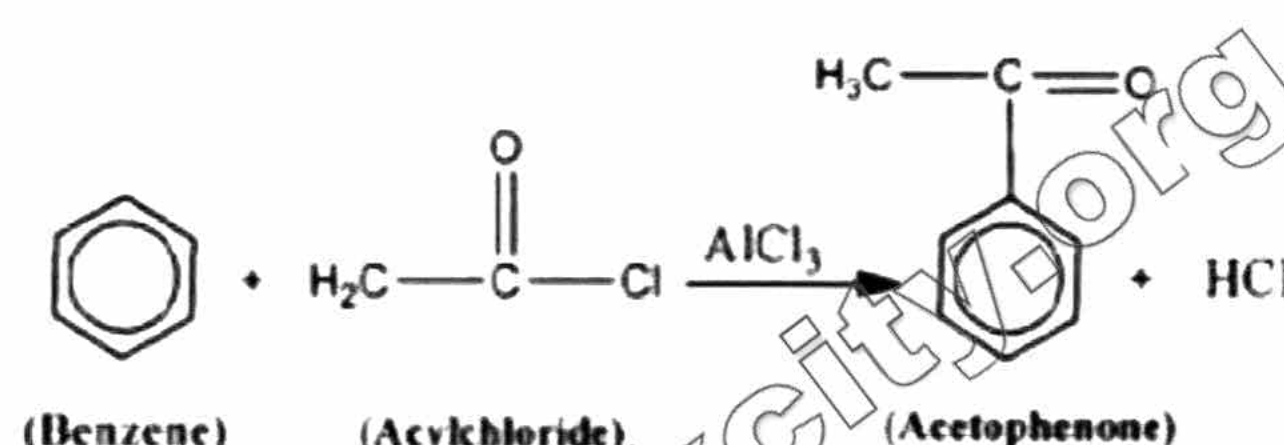
Oxidation of Alcohol

In the Oxidation of alcohols, the -OH functional groups are converted to carbonyl groups ($\text{C}=\text{O}$). Primary alcohols are oxidized to aldehydes, and secondary alcohols are oxidized to ketones, which can be achieved using pyridinium chlorochromate (PCC) as an oxidizing agent. However, tertiary alcohols do not undergo oxidation. This controlled process is valuable in obtaining specific carbonyl compounds in organic synthesis.



Friedel-Craft Acylation of Aromatic Compounds

Aromatic ketones can be synthesized through the Friedel Craft acylation method. In this reaction, an acyl chloride reacts with benzene or its derivatives in the presence of a Lewis acid catalyst, typically aluminum chloride (AlCl_3).



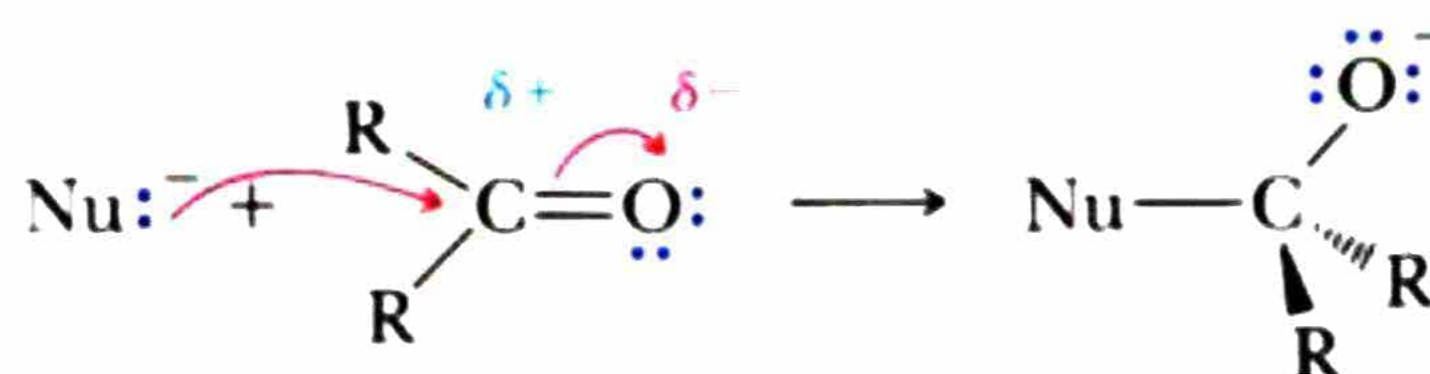
REACTIONS OF ALDEHYDE AND KETONES

Aldehyde and ketone undergo following types of reactions.

- (i) Nucleophilic addition reactions
- (ii) Reduction reaction
- (iii) Oxidation reaction

Nucleophilic addition reaction

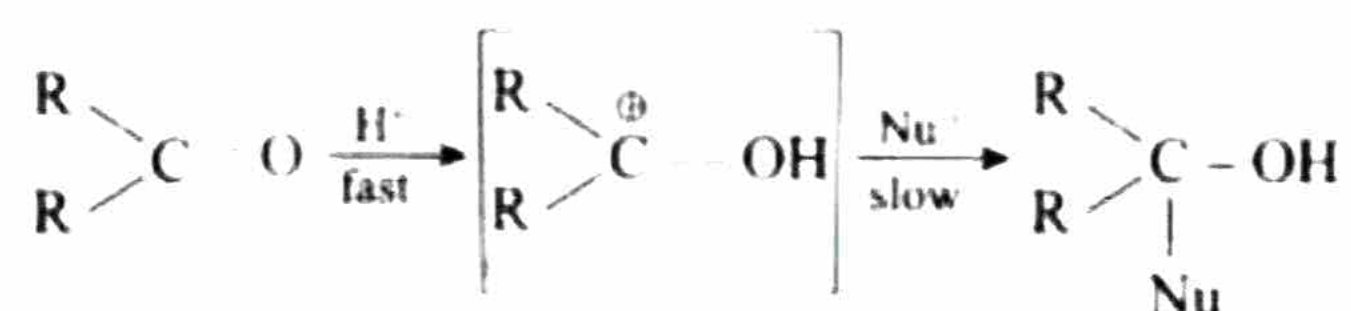
In these reactions, nucleophiles attack the carbonyl carbon of aldehydes and ketones, leading to a change in the hybridization of the carbon atom from sp^2 to sp^3 . The pi electron pair of C=O shifts towards the oxygen atom, forming an alkoxide intermediate, which is subsequently protonated to yield the addition product.



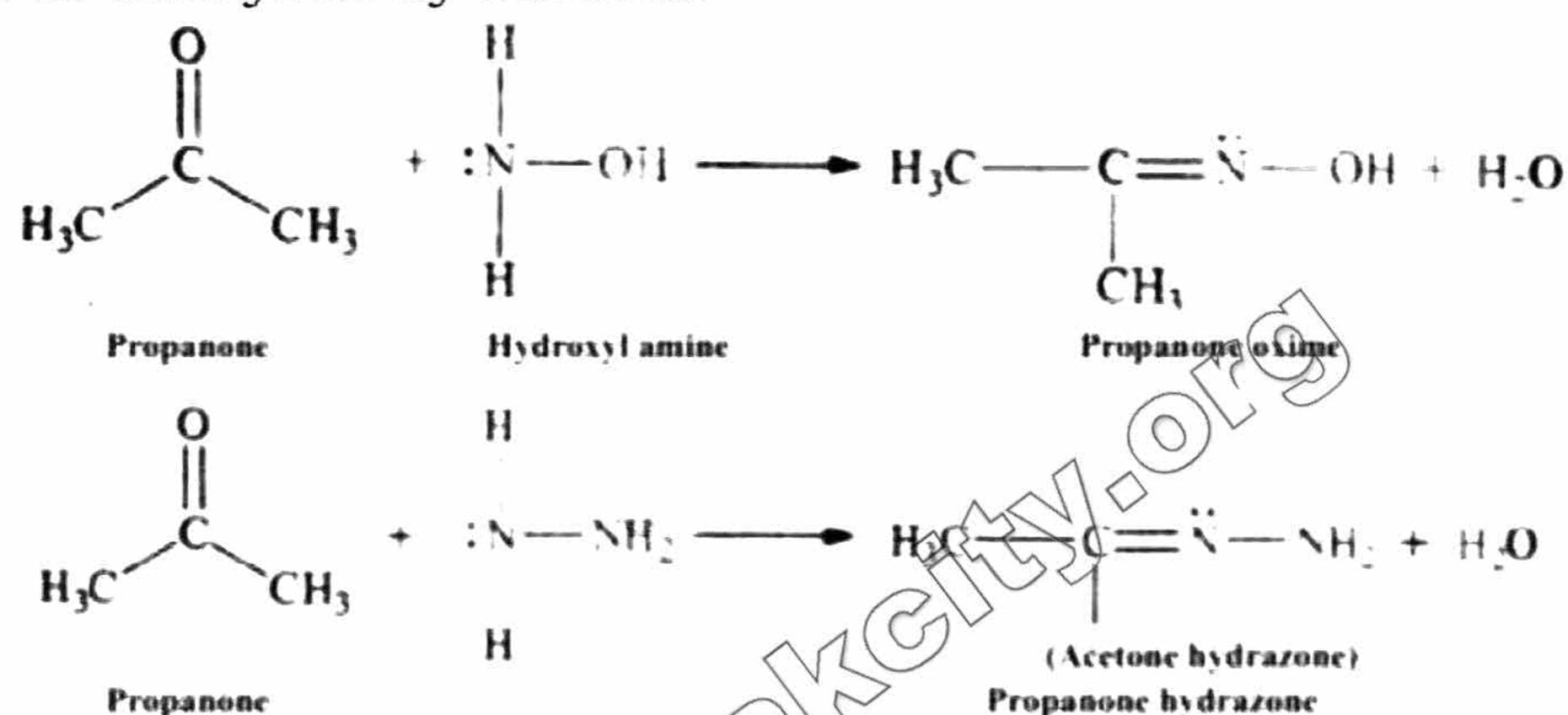
Nucleophilic addition reactions can be either acid-catalyzed or base-catalyzed, depending on the nature of reactants and the reaction conditions.

(i) Acid catalysed Nucleophilic addition reactions

An acid catalyst is employed in a case where a carbonyl compound reacts with weak nucleophile for addition. The acidic proton, attacks the carbonyl atom, resulting in the formation of a protonated carbonyl group. The general mechanism of acid catalyzed nucleophilic addition on aldehyde and ketone is written as.

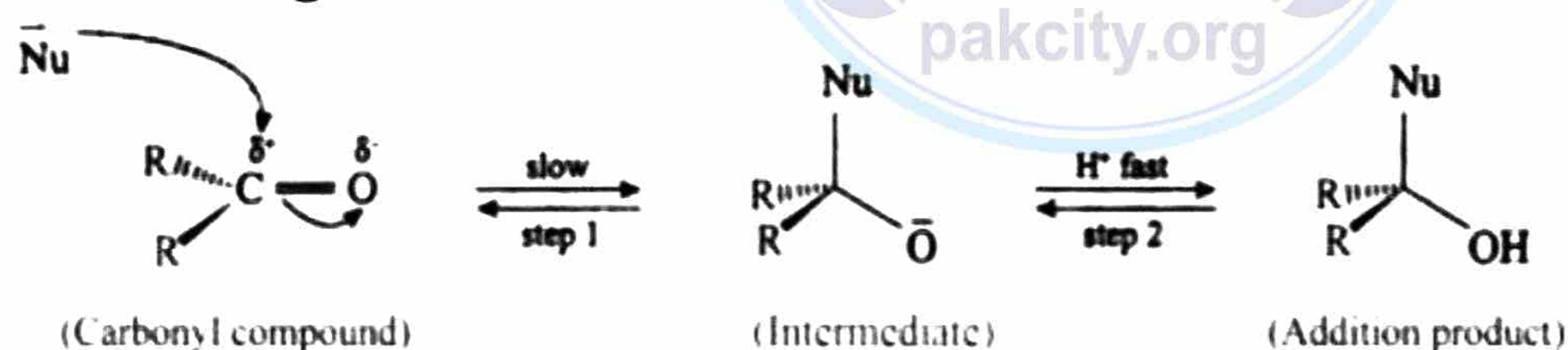


Addition of hydrazine ($\text{NH}_2\text{-NH}_2$) and hydroxyl amine ($\text{NH}_2\text{-OH}$) on aldehyde and ketone is catalyzed by an acid.

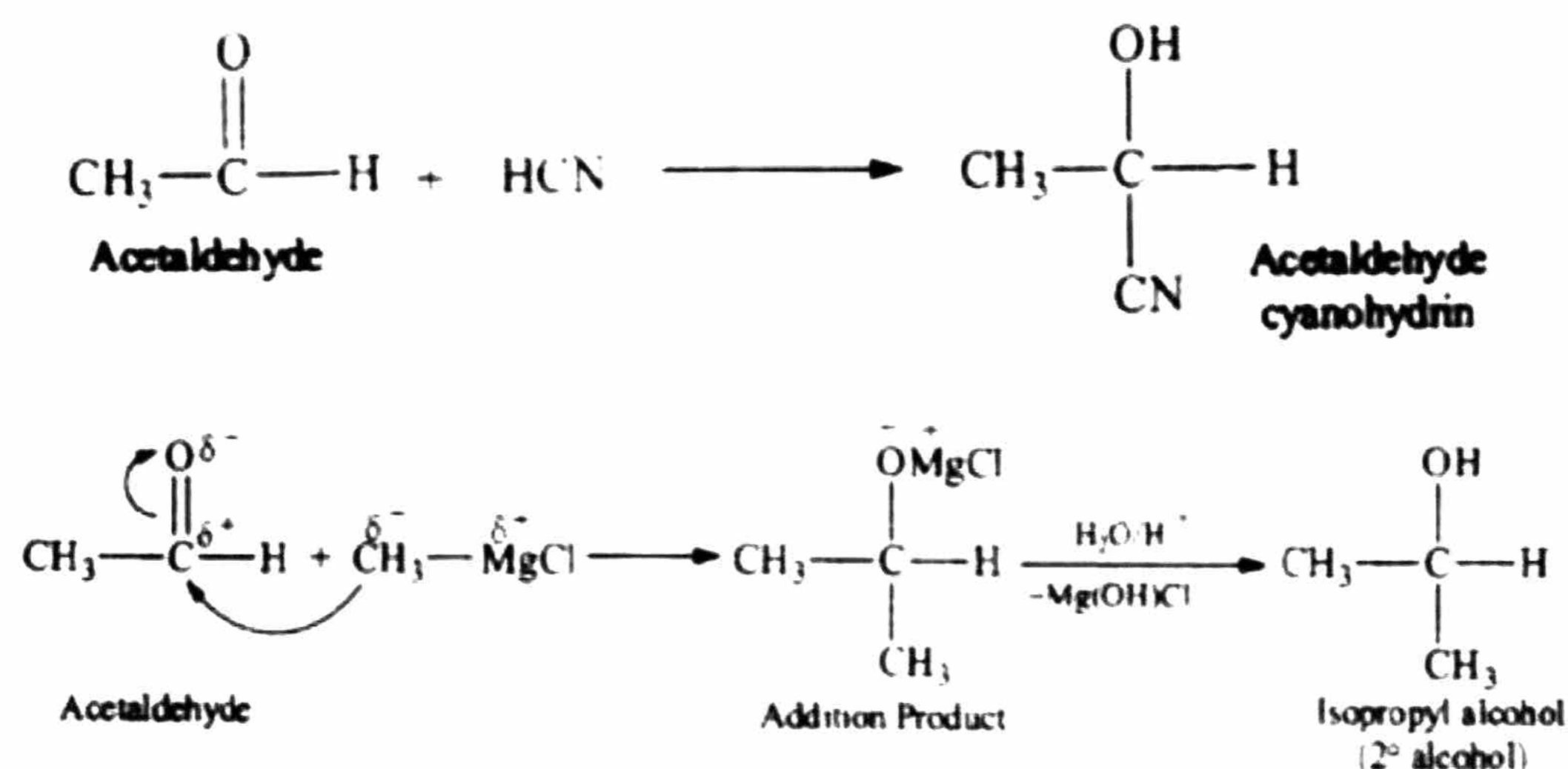


(ii) Base catalyzed Nucleophile addition reaction

Addition of strong nucleophilic reagents on aldehyde and ketone is catalysed by base. The base first reacts with the reagent to generate a nucleophile. The nucleophile then attacks on carbonyl carbon. The pi electron of C-O is then shifted towards oxygen atom to form tetrahedral alkoxide ion as intermediate. These intermediate captures a proton or the electrophile to give the product. General mechanism of base catalyzed Nucleophilic addition reaction is given as.



Addition of HCN and Grignard reagent is catalysed by base.

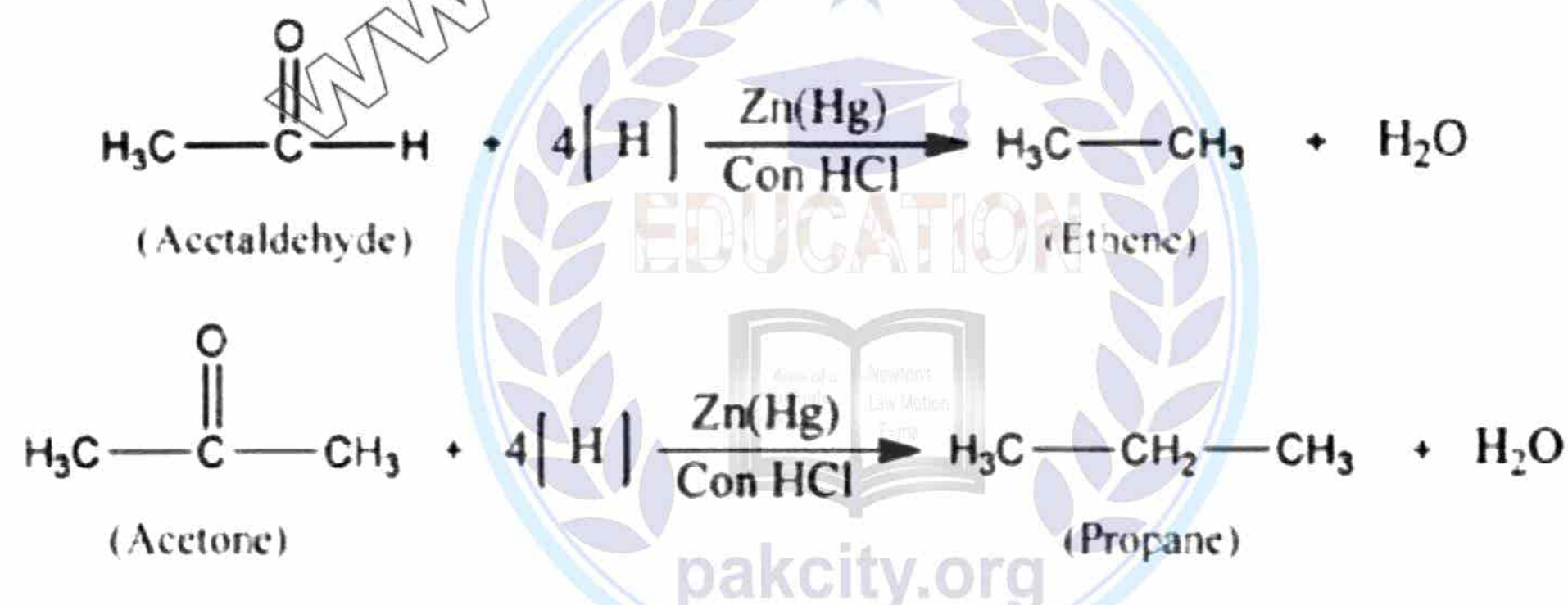


Reduction of Aldehyde and Ketone

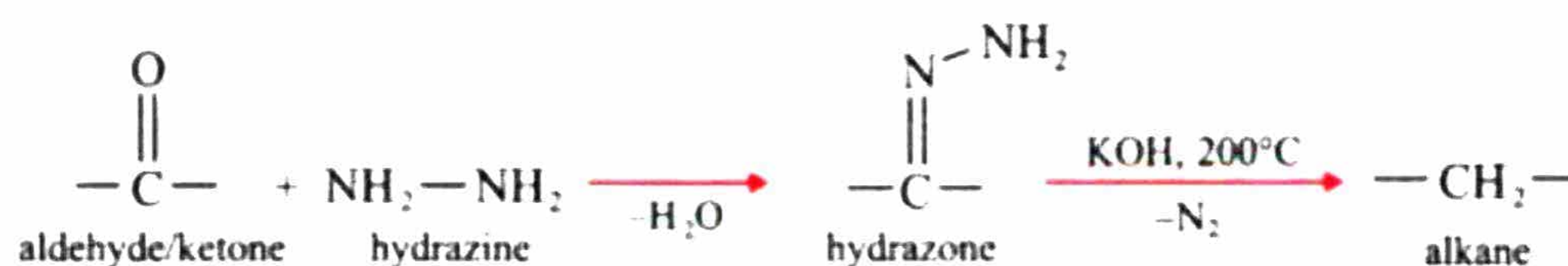
The reduction of aldehydes and ketones involves the addition of hydrogen to the carbonyl group resulting in the formation of an alkane or alcohol depending upon the suitable reducing agent used in the reaction.

Reduction to Hydrocarbon

The reduction of aldehyde and ketone into saturated hydrocarbons is carried out if a mixture of zinc amalgam and concentrated HCl is used. This is known as Clemmensen reduction.

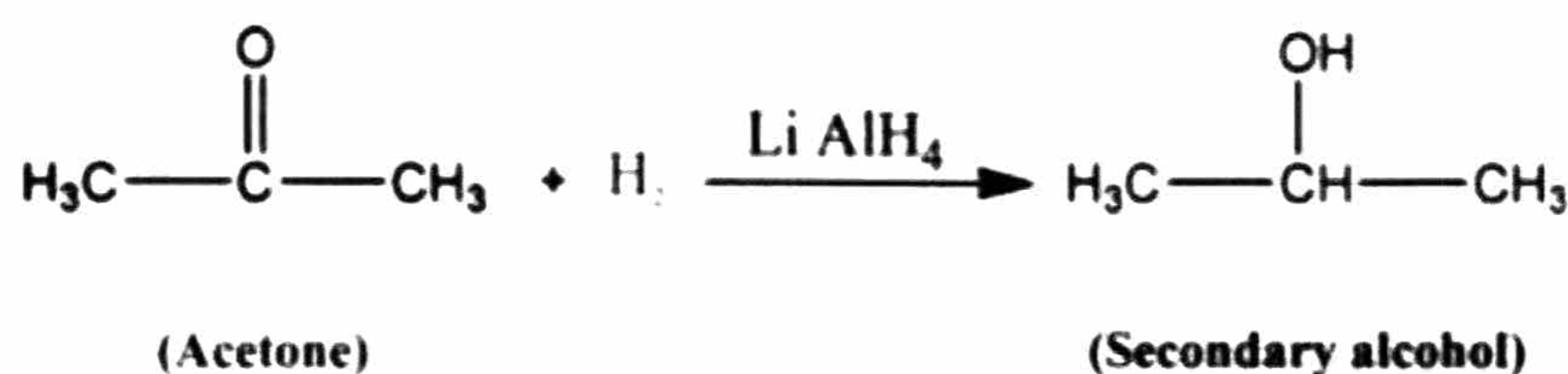
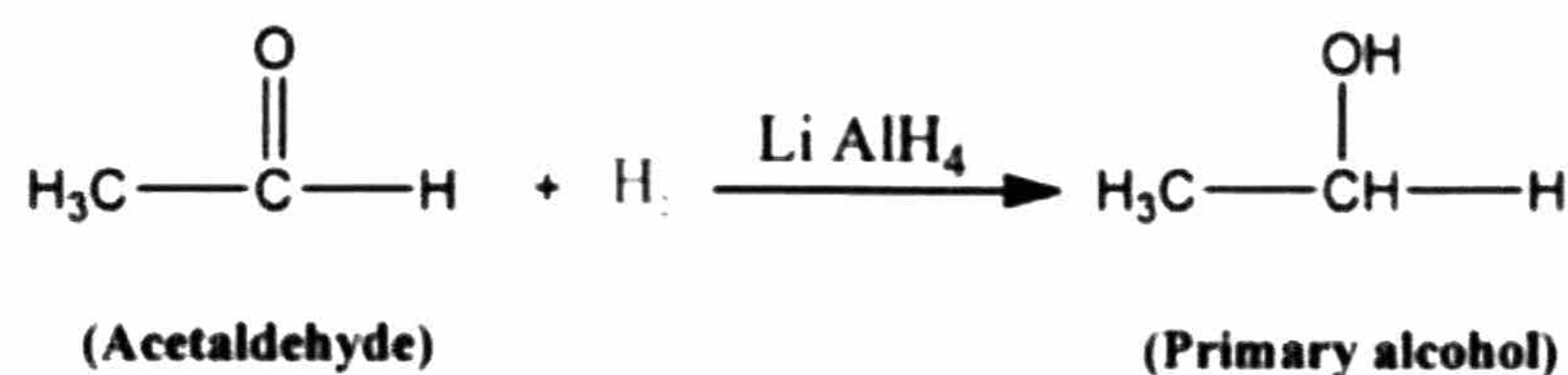


Aldehyde and ketone can also be converted into alkane by using hydrazine ($\text{NH}_2\text{-NH}_2$) and potassium hydroxide. This is known as Wolf Kishner reaction.



Reduction to Alcohol

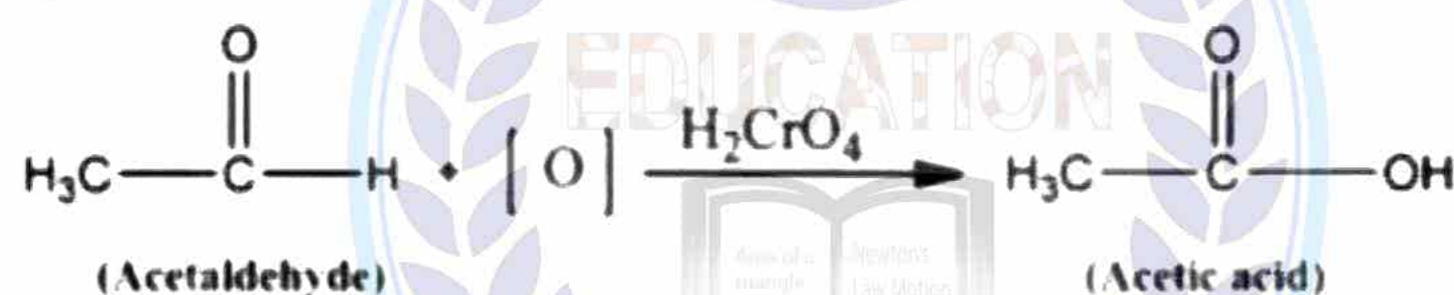
Aldehyde and ketone when treated with strong reducing agents such as NaBH_4 or LiAlH_4 , they reduce into primary and secondary alcohols respectively.



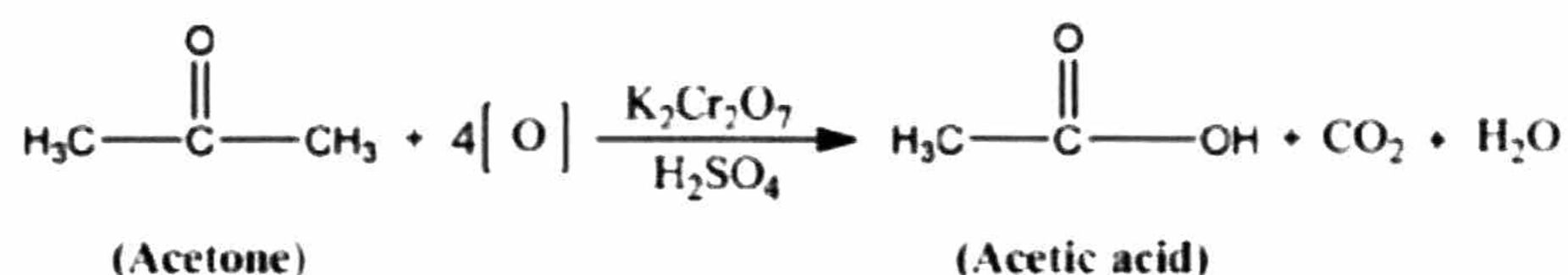
Oxidation Reaction

Aldehydes and ketones undergo oxidation with an oxidizing agent to give carboxylic acid. However, the reactivity of aldehyde towards oxidation reaction is quite easy due to the availability of active hydrogen atom at the carbonyl position, thus

- i. A variety of mild oxidizing agents such as chromic acid (H_2CrO_4), Tollen's reagent, Fehling reagent and Benedict reagent can be used to convert aldehyde into corresponding carboxylic acid. Aldehydes can also be Oxidized by strong oxidizing agents.



- ii. Oxidation of ketone is relatively slow and it involves the breaking of carbon-carbon sigma bond and it happens only in the presence of strong oxidizing agent.



Laboratory test to distinguish between aldehydes and ketones

(i) Silver mirror test

The reagent used for this test is ammoniacal silver nitrate (Tollen's reagent). Since this reagent has short shelf life, it should be freshly prepared in laboratory by mixing silver nitrate and ammonium hydroxide.

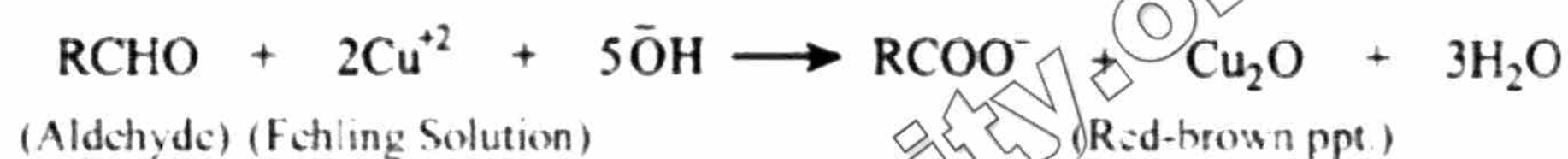


While performing the test, Tollen's reagent is mixed with the given carbonyl compound and heated to boiling. If aldehyde is present, a silver mirror will form on the inside of the test tube.

(ii) Fehling test

There are two Fehling solutions available in laboratory. Fehling A is an aqueous copper (II) sulphate solution while Fehling B is an aqueous solution of sodium hydroxide (NaOH) with sodium potassium tartrate.

To carry out the Fehling's test, mix equal volumes of Fehling A and B in a test tube, heat the mixture to boiling and then add a small amount of given carbonyl compound into the test tube. If aldehyde is present, the blue colour of Fehling solution (Cu^{2+}) changes to red precipitates (ppt) of copper (I) oxide.



Difference between Aldehyde and Ketone

Basic Structure:

Both aldehydes and ketones are carbonyl compounds but in aldehydes, the carbonyl carbon is attached with at least one alkyl or aryl group while in ketones, carbonyl carbon is attached with two alkyl or aryl groups.

Physics Properties:

The boiling point of ketones is relatively higher than aldehydes since carbonyl group of ketones is more polarized than aldehydes.

Reactivity:

The reactivity of aldehydes towards nucleophilic addition is greater than ketones because of less steric hindrance and less electronic effect.

Oxidation into Carboxylic acid:

Ketones oxidize to carboxylic acid with strong oxidizing agent such as potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and potassium permanganate (KMnO_4) while aldehydes can easily be oxidized to carboxylic acid with mild oxidizing agent such as chromic acid (H_2CrO_4), Tollen's reagent and Fehling solution and Benedict solution.

Reduction into alcohol:

Reduction of aldehydes in the presence of strong reducing agents such as lithium aluminum hydride (LiAlH_4) and sodium borohydride (NaBH_4) gives primary alcohol while the reduction of ketones gives secondary alcohol.

Some applications of aldehydes and ketones

Application	Aldehydes	Ketones
Organic Synthesis	Used as key intermediates in various organic reactions.	Important starting materials for creating complex organic compounds.
Flavor Fragrance	Provide characteristic aroma and taste to many natural and synthetic products, e.g., vanillin and benzaldehyde.	Used as flavouring agents and fragrances in the food, cosmetic, and perfume industries.
Pharmaceuticals	Serve as building blocks for some various pharmaceuticals, such as anti-inflammatory drugs and antihistamines.	ketones are used as active pharmaceutical ingredients in medicines.
Solvents	Formaldehyde is used as solvent for certain reactions.	Acetone is a widely used a solvent for chemical reactions and as a nail polish remover.

Short Questions

1. Give reasons for the following:

i. The boiling point of aldehydes and ketones is lower than alcohol.

Aldehydes and ketones have **weaker intermolecular forces** compared to alcohols. Here's why:

- **Alcohols:** Possess an -OH group, enabling **hydrogen bonding** between molecules. These hydrogen bonds are strong and require significant energy to break, leading to a **higher boiling point**.
- **Aldehydes and Ketones:** Contain a carbonyl group (C=O) but lack the -OH group. This absence prevents hydrogen bonding. Instead, they rely on weaker **dipole-dipole interactions** for intermolecular attraction. These weaker forces require less energy to overcome, resulting in a **lower boiling point** compared to alcohols.

ii. Formaldehyde is highly soluble in water as compared to other aldehydes.

High Water Solubility of Formaldehyde:

Formaldehyde (HCHO) has a significantly higher water solubility compared to other aldehydes due to its **smaller size and the presence of two hydrogen atoms** in its functional group:

- **Smaller size:** Formaldehyde has the simplest aldehyde structure (HCHO). With a smaller molecule, there's a greater surface area available for hydrogen bonding with water molecules, leading to higher solubility.
- **Two hydrogen atoms:** Formaldehyde has two hydrogens directly attached to the oxygen atom (O) in the carbonyl group. These hydrogens can participate in more extensive hydrogen bonding with water compared to aldehydes with only one hydrogen on the O atom.

iii. Oxidation of aldehydes is faster than ketones.

Oxidation Rate of Aldehydes vs. Ketones:

i. **Faster Oxidation of Aldehydes:**

Aldehydes generally undergo oxidation reactions **faster** than ketones. This can be attributed to several factors:

- **More reactive carbonyl carbon:** In aldehydes, the carbonyl carbon atom has only one bulky substituent (a hydrogen) attached. This allows for easier access by the oxidizing agent to the carbon-oxygen double bond, facilitating oxidation.
- **Formation of a more stable intermediate:** During oxidation, aldehydes form a resonance-stabilized intermediate (a gem-diol) due to the presence of two hydrogens on the carbonyl carbon. This

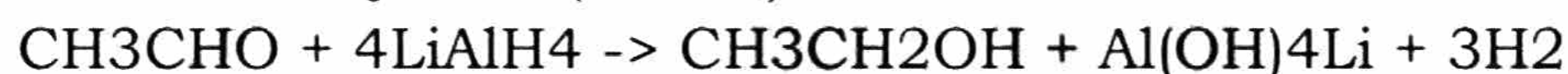
intermediate is more stable than the corresponding intermediate formed in ketone oxidation, lowering the activation energy barrier and speeding up the reaction.

2. Write the equation for the reaction of acetaldehyde with the following:

i. Chromic acid (H_2CrO_4)



ii. Lithium Aluminum hydride (LiAlH_4)



ii. Zinc mercury amalgam

3. How is formaldehyde prepared by ozonolysis?

Notes

4. Why is formaldehyde more reactive towards Nucleophilic addition reactions compared with ketones.

Formaldehyde exhibits greater reactivity towards nucleophilic addition reactions compared to ketones due to two key factors:

1. Steric Hindrance:

- **Formaldehyde:** Has only one hydrogen atom attached to the carbonyl carbon ($\text{C}=\text{O}$). This results in **less steric hindrance** around the electrophilic carbon center. Nucleophiles can approach and attack this carbon more easily due to the absence of bulky substituents.
- **Ketones:** Contain two bulky substituent groups (alkyl or aryl groups) attached to the carbonyl carbon. This creates **more steric hindrance** around the electrophilic carbon. The bulky groups can physically hinder the nucleophile's approach and make the reaction slower.

2. Electronic Effect:

- **Formaldehyde:** The presence of two hydrogen atoms bonded to the oxygen atom in the carbonyl group creates a **greater electron-withdrawing effect** through inductive electron donation. This effect pulls electron density away from the carbon-oxygen double bond, making the **carbonyl carbon more positive (electrophilic)**. A more positive carbon is more attractive to electron-rich nucleophiles.
- **Ketones:** Generally have only one alkyl group attached to the oxygen atom. This group's electron-withdrawing effect is weaker compared to two hydrogens in formaldehyde. Consequently, the carbonyl carbon in ketones is **slightly less positive** than in formaldehyde, leading to a lower electrophilic character and reduced reactivity towards nucleophiles.

In summary, the combination of less steric hindrance and a more electrophilic carbonyl carbon makes formaldehyde a more reactive nucleophile acceptor compared to ketones. This allows for faster and more efficient nucleophilic addition reactions with formaldehyde.

5. How does the oxidation of ketones differ from the oxidation of aldehydes?

The key differences between the oxidation of ketones and aldehydes lie in the ease of oxidation and the products formed:

Ease of Oxidation:

- **Aldehydes (RCHO):** Generally much **easier to oxidize** than ketones. This is due to the presence of a more reactive carbonyl carbon atom.
 - **Reason:** In aldehydes, the carbonyl carbon has only one bulky substituent (a hydrogen atom). This allows for easier access by oxidizing agents to the carbon-oxygen double bond, facilitating oxidation.
- **Ketones (R₂CO):** Considerably **more resistant to oxidation** compared to aldehydes.
 - **Reason:** Ketones have two bulky substituents on the carbonyl carbon, creating steric hindrance. This hindrance makes it more difficult for oxidizing agents to approach and attack the carbon-oxygen double bond.

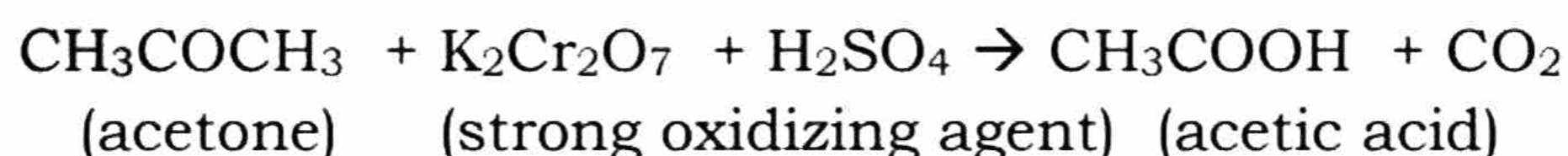
Products of Oxidation:

- **Aldehydes:** When oxidized, aldehydes are readily converted to **carboxylic acids (RCOOH)**. This process involves the breaking of the carbon-hydrogen bond in the carbonyl group and the addition of an oxygen atom (from the oxidizing agent) to form a new C-O bond.

Example: CH_3CHO (acetaldehyde) + $\text{O}_2 \rightarrow \text{CH}_3\text{COOH}$ (acetic acid)

- **Ketones:** Cleavage of the carbon-carbon bond adjacent to the carbonyl group is the typical mode of oxidation for ketones under harsher conditions (strong oxidizing agents and often heat). This cleavage results in the formation of a carboxylic acid with a smaller carbon chain and another carboxylic acid or a ketone with a shorter chain depending on the position of the cleavage.

Example:



6. Why are ethers considered as good solvents in organic reactions?

- **Polarity:** The polar nature allows them to solvate (dissolve) other polar molecules through dipole-dipole interactions.

- **Hydrogen Bonding Acceptance:** Enables interaction with a broader range of organic compounds containing O-H or N-H groups.
- **Inertness:** Minimizes interference with the desired reaction.
- **Moderate Water Solubility:** Provides versatility for reactions involving water or water-soluble components.
- **Volatility:** Facilitates solvent removal after the reaction.

Descriptive Questions

1. What are aldehydes and ketones? Describe the structure and type of hybridization in them.

Notes

2. Explain the acid-catalyzed and base-catalyzed nucleophilic addition reactions in aldehydes and ketones.

Notes

3. Describe how aldehydes are distinguished from ketones by the following laboratory test.

(i) Tollen's reagents (ii) Fehling solution

Notes

4. Write the equation and give the name of major product in the following chemical process.

- Oxidation of acetone with acidified $K_2Cr_2O_7$.
- Reduction of acetaldehyde with $NaBH_4$.
- Hydration of ethyne in the presence of $H_2SO_4/HgSO_4$
- Acylation of benzene in the presence of $AlCl_3$.

5. Give four differences between aldehydes and ketones.

Notes

6. Write the equation for the nucleophilic addition reaction if formaldehyde treated with

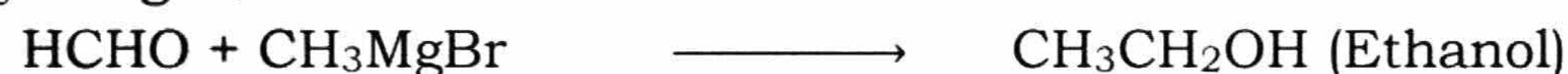
i. Hydrogen cyanide



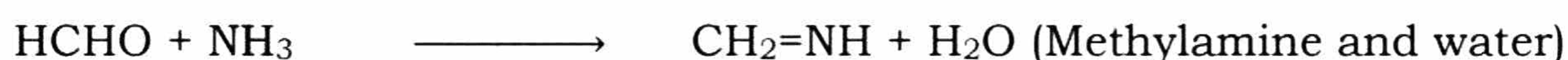
ii Primary alcohol



iii. Methyl magnesium bromide



iv. Ammonia



7. Explain the factors that influence the reactivity of carbonyl compounds towards nucleophilic addition reaction.

Notes