CHAPTER 8 CARBOYNL COMPOUNDS 1: ALDEHYDES AND KETONES

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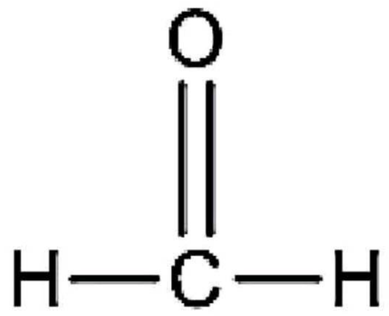
Carbonyl Compounds:

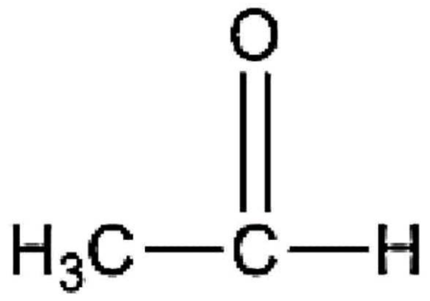
Those compounds which contain carbonyl group (-CO-) are called carbonyl compounds.

Aldehydes and ketones are included in carbonyl compounds.

Aldehydes contains (-COH) Functional group and their general formula is R-COH.

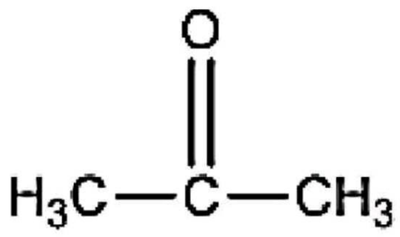


(Formoldehyde)

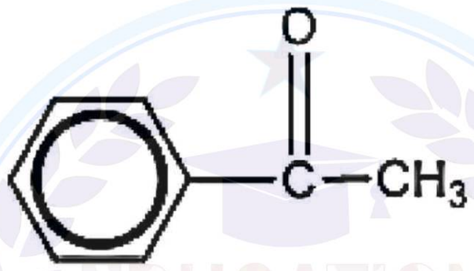


(Acetaldehyde)

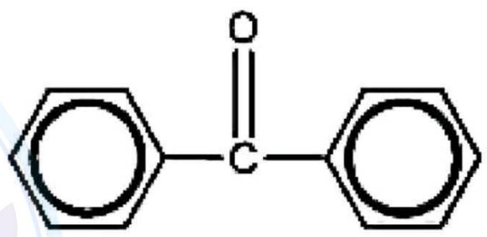
Ketones contains (-COR) functional group and their general formula is R-COR.



(Acetone)



(Acetophenone)



(Benzophenone)

Physical Properties of Aldehyde:

- Methanal and ethanal are gases, other aldehydes are colorless liquids and aldehydes with more than 20 carbon atoms are solids at room temperature.
- Most of the ketones are liquids and ketones with more than 20 carbon atoms are solids.
- Lower aldehydes have a pungent smell whereas ketones and higher aldehydes have a pleasant smell.
- Carbonyl compounds have higher boiling point than alkanes due to polarity but they have lesser boiling points than alcohols or carboxylic acids due to the absence of hydrogen bond.
- Carbonyl compounds are soluble in water due to their polar nature. Solubility decreases with increase in carbon atoms.

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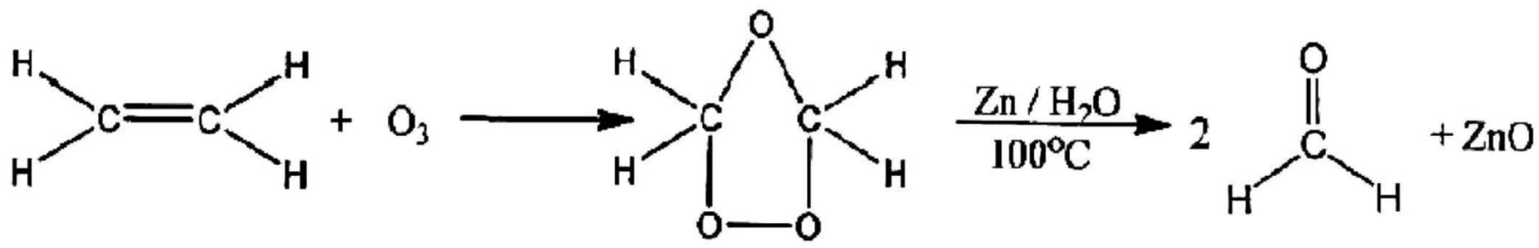
PREPARATION OF ALDEHYDE AND KETONE

1. OZONOLYSIS OF ALKENES



(Ethene) (Ozonide) (Formaldehyde)

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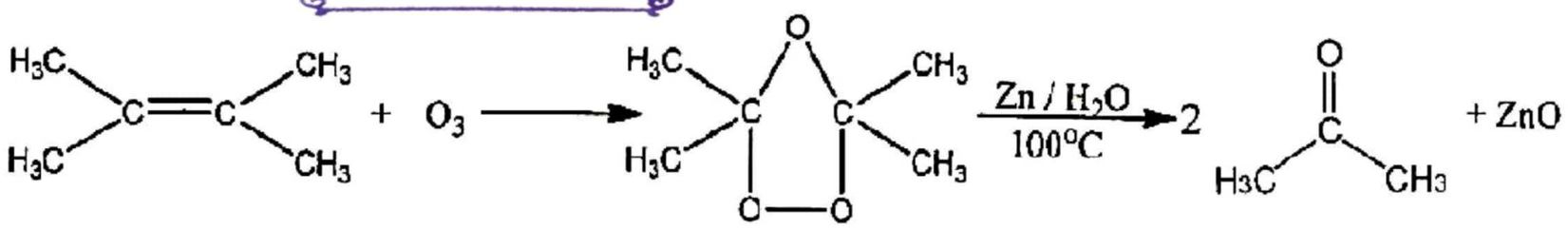
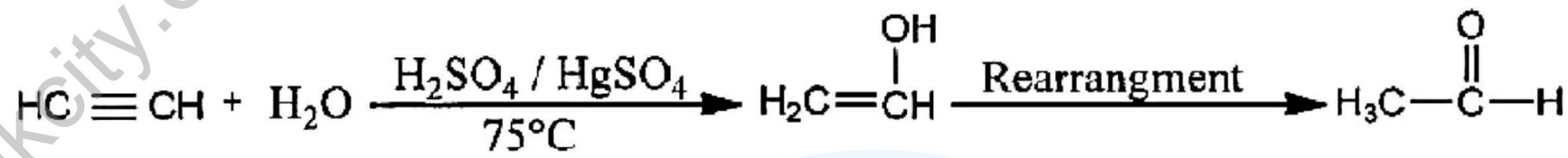


(2, 3-dimethyl butene) (Ozonide) (Acetone)

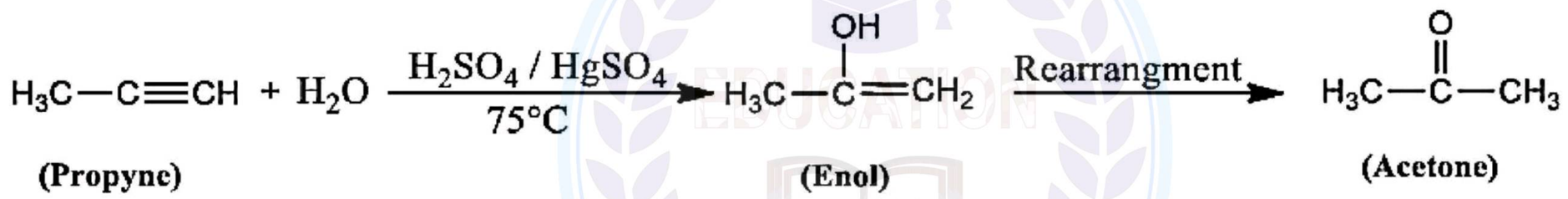
2. HYDRATION OF ALKYNE

(i) The hydration of ethyne gives acetaldehyde



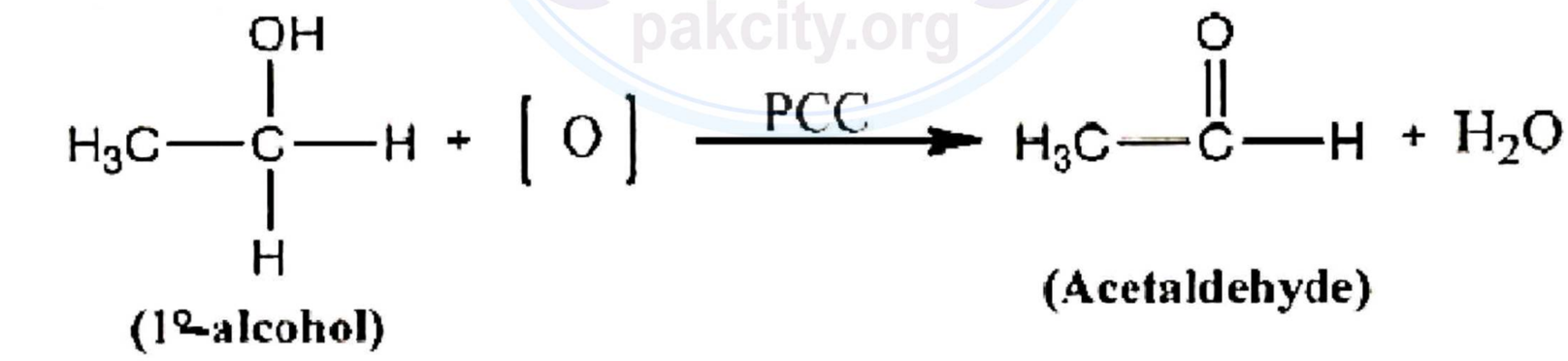
(Ethyne) (Enol) (Acetaldehyde)

(ii) The hydration of propyne gives propanone

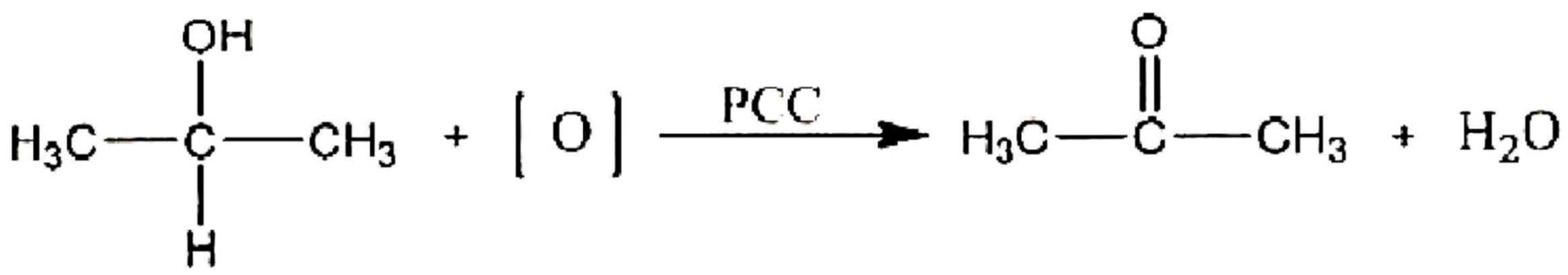


(Propyne) (Enol) (Acetone)

3. OXIDATION OF ALCOHOL



(1°-alcohol) (Acetaldehyde)



(2°-alcohol) (Acetone)

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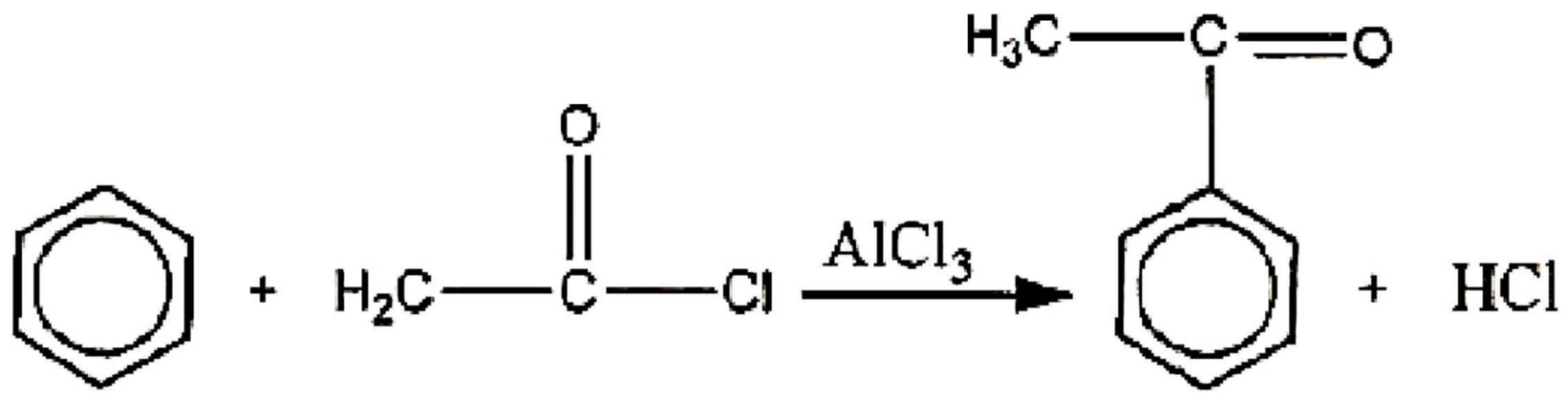
4. FRIEDEL-CRAFT'S ACYLATION OF AROMATIC COMPOUNDS



(Benzene) **(Acylchloride)** **(Acetophenone)**

REACTIONS OF ALDEHYDE AND KETONES

Aldehyde and ketone undergo following types of reactions.

(i) Nucleophilic addition reactions

(ii) Reduction reaction

(iii) Oxidation reaction

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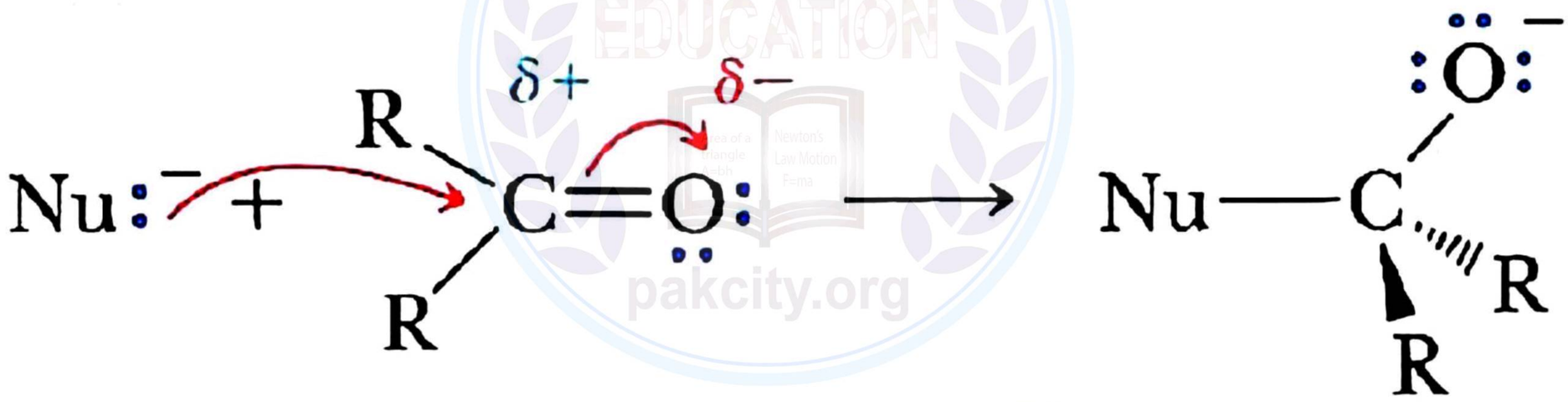
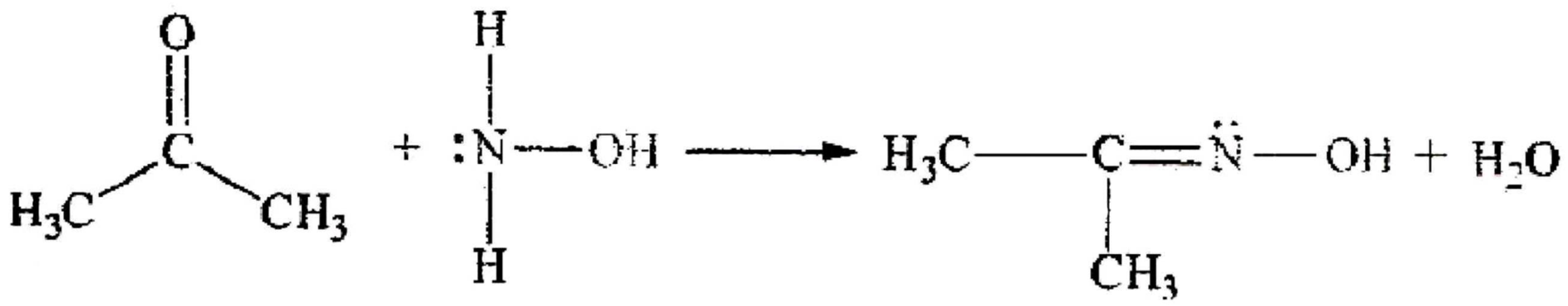
1 Nucleophilic addition reaction

In this reaction a nucleophile attacks the carbonium ion by the cleavage of pi bond. The hybridization of carbon atom changes from sp^2 to sp^3.

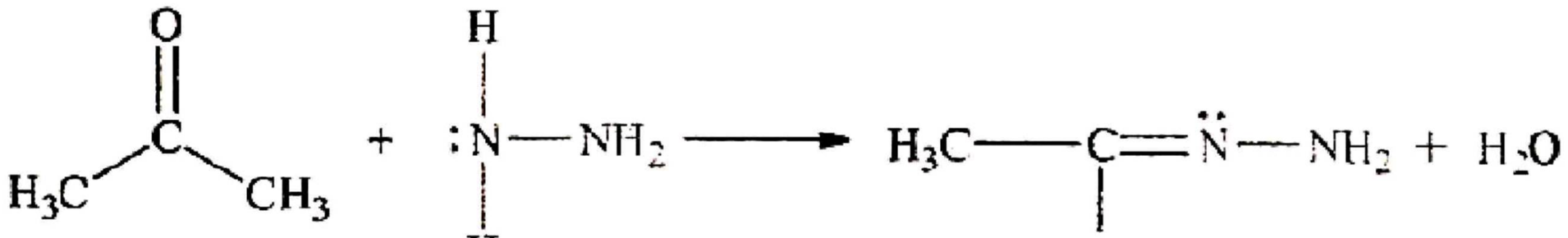


a) Reaction with hydroxyl amine (NH_2-OH)



Propanone **Hydroxyl amine** **Propanone oxime**

b) Reaction with hydrazine (NH_2-NH_2)



Propanone **(Acetone hydrazone)** **Propanone hydrazone**

c) Reaction with HCN

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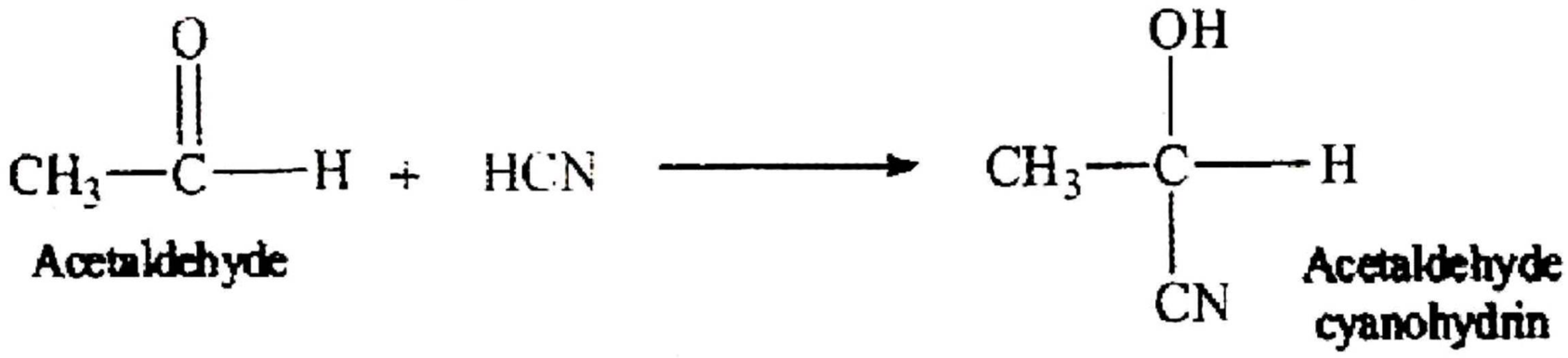
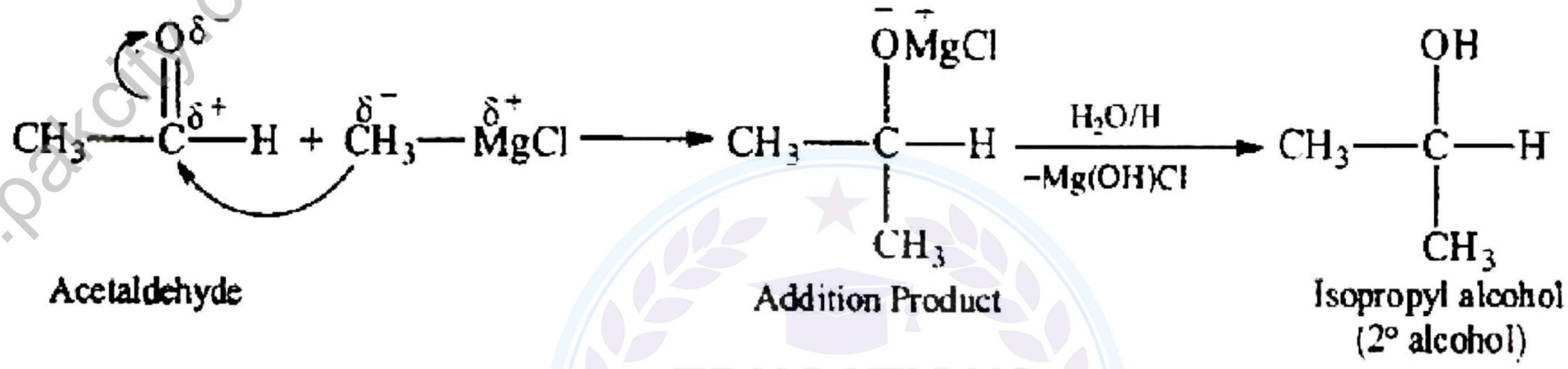


Acetaldehyde **Acetaldehyde cyanohydrin**

d) Reaction with Grignard's Reagent



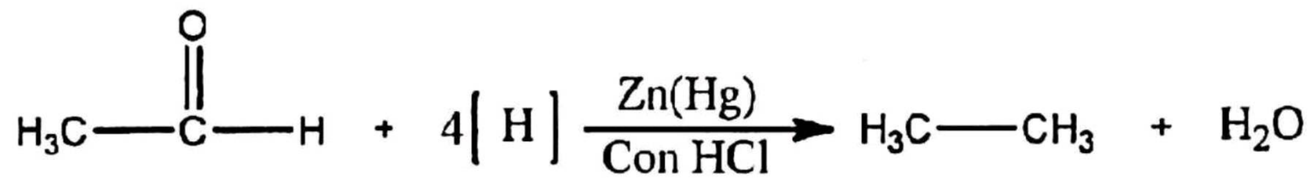
Acetaldehyde **Addition Product** **Isopropyl alcohol (2° alcohol)**

2 Reduction of Aldehyde and Ketone

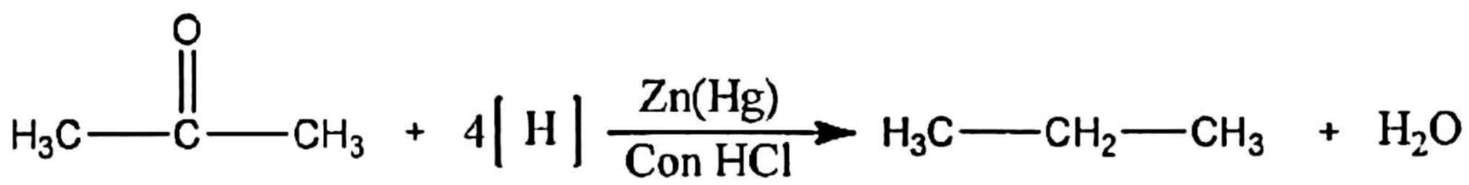
1. Reduction to Hydrocarbon

(a) Clemmensen Reduction

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.



(Acetaldehyde) (Ethene)



(Acetone) (Propane)

(b) Wolf Kishner Reduction

Aldehyde and ketone can also be converted into alkane by using hydrazine (NH2-NH2) and postassium hydroxide. This is known as Wolf Kishner reaction.

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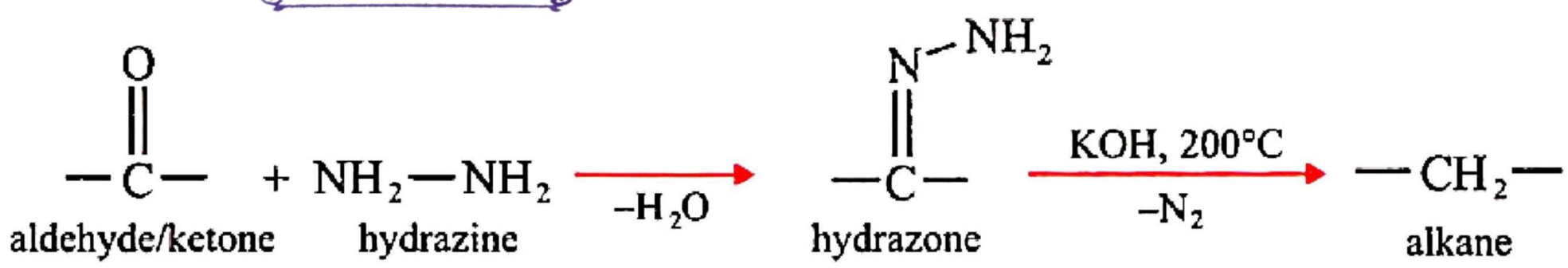
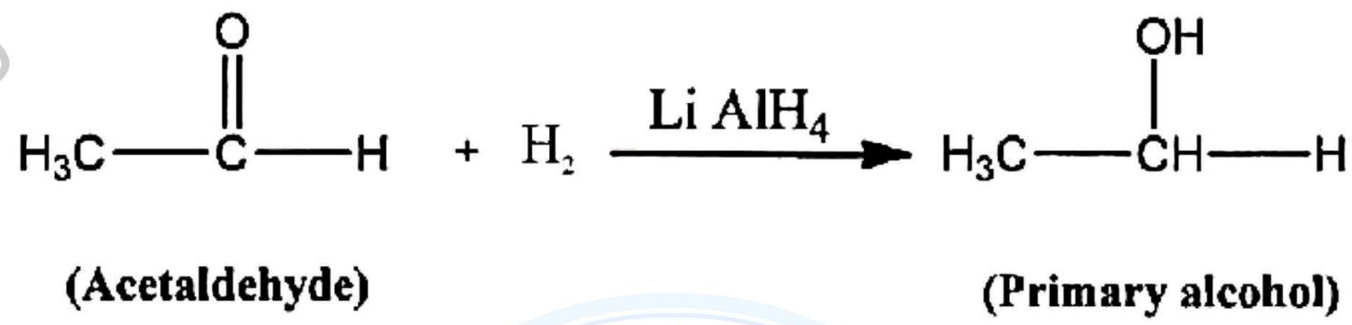
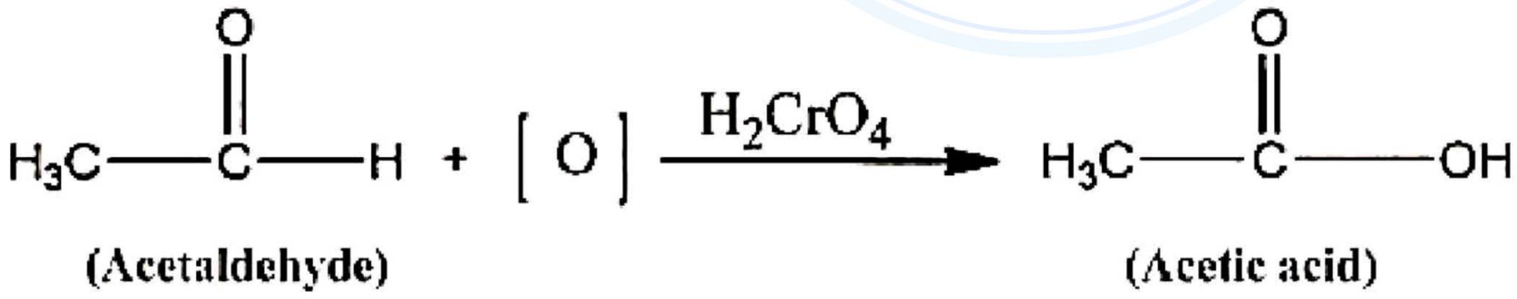


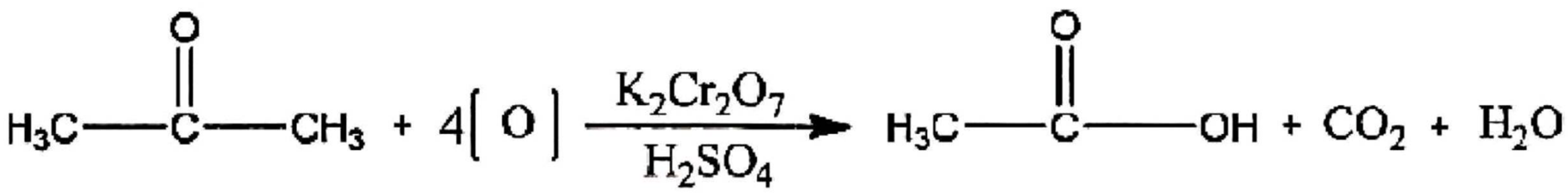
2. Reduction to Alcohol

In this reaction, a reducing agent is used such as $NaBH_4$ or $LiAlH_4$.



3 Oxidation Reaction





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.

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$$RCHO + 2[Ag(NH_3)_2]OH \xrightarrow{\text{Heat}} RCOO^-NH_4^+ + 3NH_3 + H_2O + 2Ag\downarrow$$

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).

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 color of Fehling solution (Cu^{+2}) changes to red precipitates (ppt) of copper (I) oxide.

$$\underset{\text{(Aldehyde)}}{RCHO} + \underset{\text{(Fehling Solution)}}{2Cu^{+2} + 5\bar{O}H} \longrightarrow RCOO^- + \underset{\text{(Red-brown ppt.)}}{Cu_2O} + 3H_2O$$

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Multiple Choice Questions

(i) Ketones when treated with $LiAlH_4$, they reduce to:
(a) Primary alcohol (b) Secondary alcohol
(c) Tertiary alcohol (d) Dihyderic alcohol

(ii) The reagent used to oxidizes ketones into carboxylic acids is:
(a) Ammoniacal silver nitrate (b) Potassium dichromatic
(c) Fehling solution (d) Benedict solution

(iii) The carbonyl carbon of aldehydes and ketones is:
(a) Sp hyrbidized (b) Sp^2 hyrbidized
(c) Sp^3 hyrbidized (d) dsp^3 hyrbidized

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(iv) Acetophenone is the member of ketone family, it contains:
(a) Two alkyl groups (b) Two aryl group
(c) One alkyl and one aryl group (d) One aryl and one hydrogen atom

(v) The most reactive molecule towards nucleophilic addition in the following is:
(a) Formaldehyde (b) Acetaldehyde
(c) Diethyl ketone (d) Acetophenone

(vi) Clemmensen reduction is the conversion of aldehydes and ketones into:
(a) Alkanes (b) Alkenes
(c) Alkyl halides (d) Alcohols

(vii) Hydration of propyne in the presence of H_2SO_4 and $HgSO_4$ gives:
(a) Formaldehyde (b) Methyl ethyl ketone
(c) Acetone (d) Acetaldehyde

(viii) Which of the following carbonyl compound is most soluble in water?
(a) Formaldehyde (b) Acetaldehyde
(c) Benzaldehyde (d) Acetophenone

(ix) Which of the following gives silver test with Tollen's reagent?
(a) HCHO (b) CH_3-O-CH_3
(c) C_2H_5OH (d) CH_3COOH

(x) On reduction of a carbonyl compound by Zn-Hg and Conc. HCl, it is converted to an alkane. This reaction is known as;
(a) Dow reduction (b) Cope reduction
(c) Clemmensen reduction (d) Wolf-Kishner reduction

Short Questions

1. Give reasons for the following:
   i. The boiling point of aldehydes and ketones is lower than alcohol.

Ans. Aldehydes and ketones do not have hydrogen bond that's why they have lower boiling point than alcohol.

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

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Ans. Form aldehyde is highly soluble in water because of the presence of only one carbon atom. The greater number of carbon atoms increases non-polar nature and hinders solubility in water.

   iii. Oxidation of aldehydes is faster than ketones.

Ans. Oxidation of aldehyde is faster than ketones due to less steric hindrance. Ketones have more steric hindrance due to the presence of alkyl radicals on both sides of carbonyl group.

2. Write the equation for the reaction of acetaldehyde with the following:
   i. Chromic acid (H_2CrO_4)
   ii. Lithium Aluminum hydride ($LiAlH_4$)
   iii. Zinc mercury amalgam

ALREADY DISCUSSED ABOVE

3. How is formaldehyde prepared by ozonolysis?

ALREADY DISCUSSED ABOVE

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

Ans. Formaldehyde is more reactive towards nucleophilic addition reactions due to less steric hindrance. Ketones have more steric hindrance due to the presence of alkyl radicals on both sides of carbonyl group that's why they have less reactivity towards nucleophilic addition reactions.

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

Oxidation into Carboxylic acid: Ketones oxidizes to carboxylic acid with strong oxidizing agent such as potassium dichromate ($K_2Cr_2O_7$) 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.

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

Ans. Ethers are considered as good solvents in organic reactions because of their inert nature.

Descriptive Questions

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

Ans. Aldehydes contains (-COH) Functional group and their general formula is R-COH.

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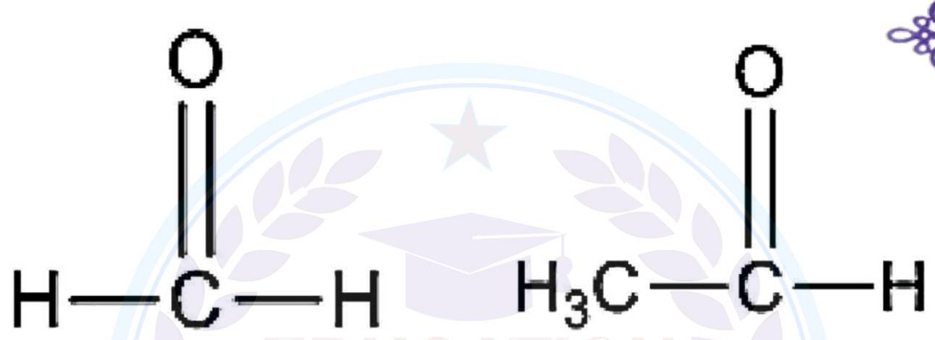
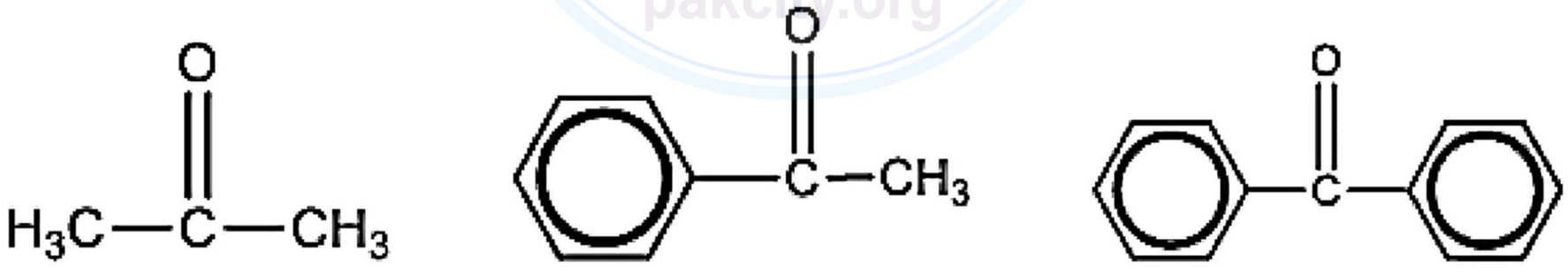


(Formoldehyde) **(Acetaldehyde)**

Ketones contains (-COR) functional group and their general formula is R-COR.



(Acetone) **(Acetophenone)** **(Benzophenone)**

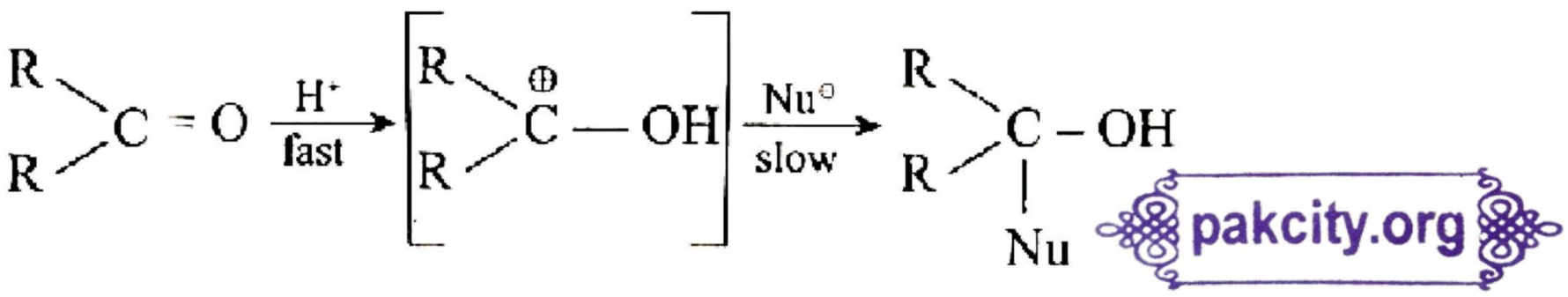
In aldehydes and ketones, the carbon atom of carbonyl group is sp^2 hybridized with a trigonal planar structure and 120° bond angle.

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

Ans.

(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. This protonation enhances the electrophilic behavior of the carbonyl carbon making it more responsive to a necleophile. Thus, a weak nucleophile can easily attack on carbonyl carbon and give the addition product. The general mechanism of acid catalysed nucleophilic addition on aldehyde and ketone is written as.



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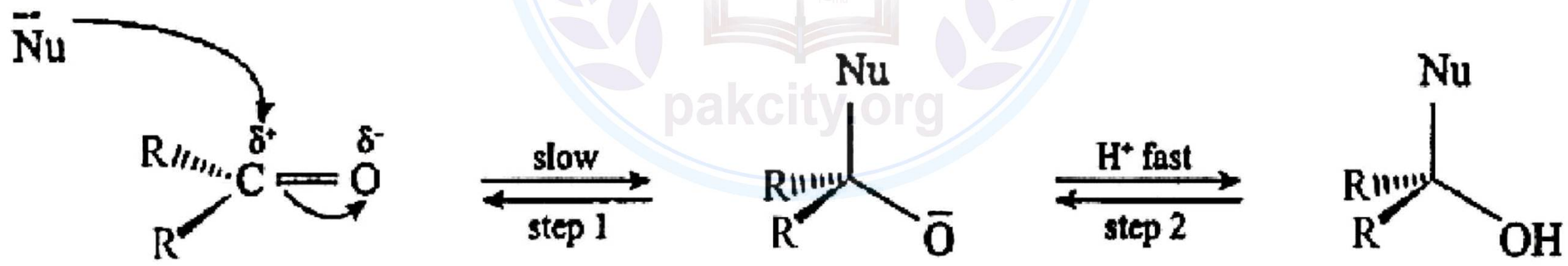
(ii) Base catalysed Nucleophilic addition reaction

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. This intermediate captures a proton or the electrophile to give the product.
General mechanism of base catalysed Nucleophilic addition reaction is given as.



(Carbonyl compound) (Intermediate) (Addition product)

3. Describe how aldehydes are distinguished from ketones by the following laboratory test.
(i) Tollen's reagents (ii) Fehling solution

ALREADY DISCUSSED ABOVE

4. Write the equation and give the name of major product in the following chemical process.
   i. Oxidation of acetone with acidified $K_2Cr_2O_7$.
   ii. Reduction of acetaldehyde with $NaBH_4$.
   iii. Hydration of ethyne in the presence of $H_2SO_4/HgSO_4$
   iv. Acylation of benzene in the presence of $AlCl_3$.

ALREADY DISCUSSED ABOVE

5. Give four differences between aldehydes and ketones.

Ans.

(1) The general formula of aldehyde is RCOH and general formula of aldehyde is RCOR.

(2) Aldehydes are more reactive than ketones.

(3) Boiling point of aldehyde is higher than aldehyde.

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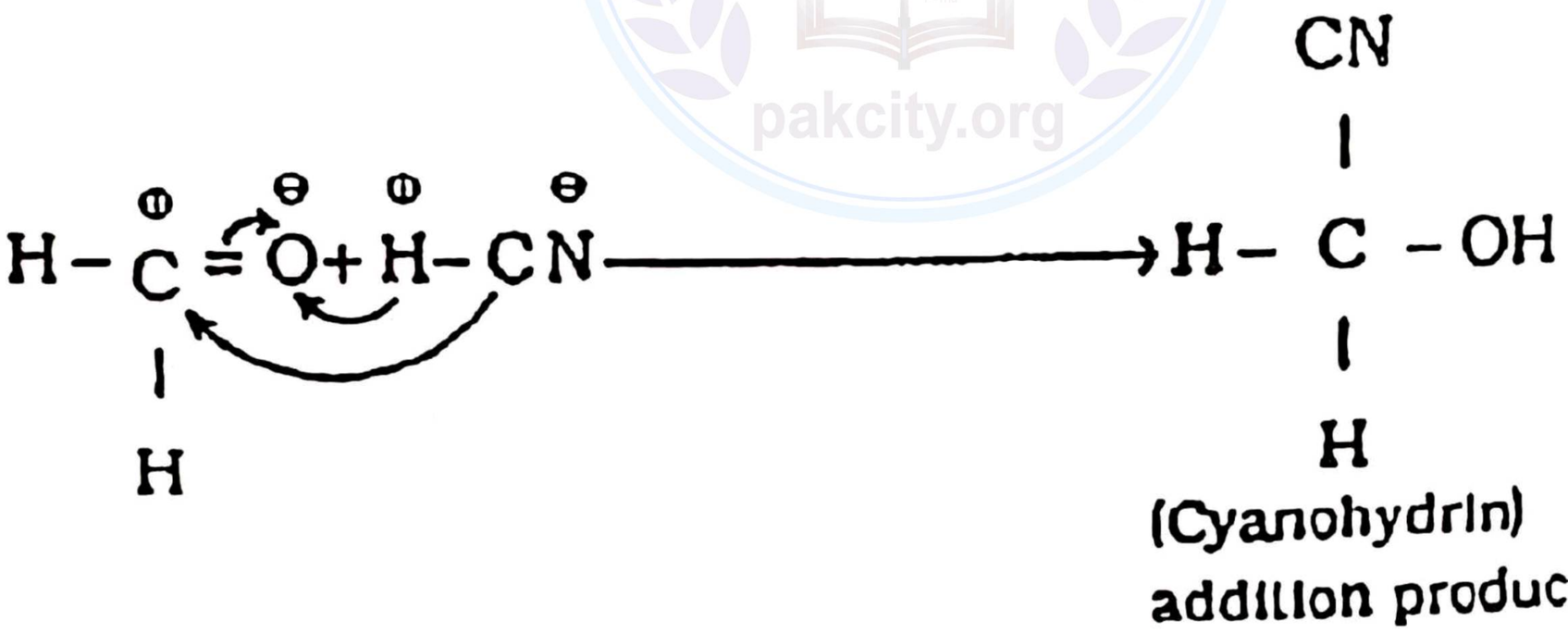
(4) Aldehydes are reduced to form primary alcohol and ketones are reduced to form secondary alcohols.

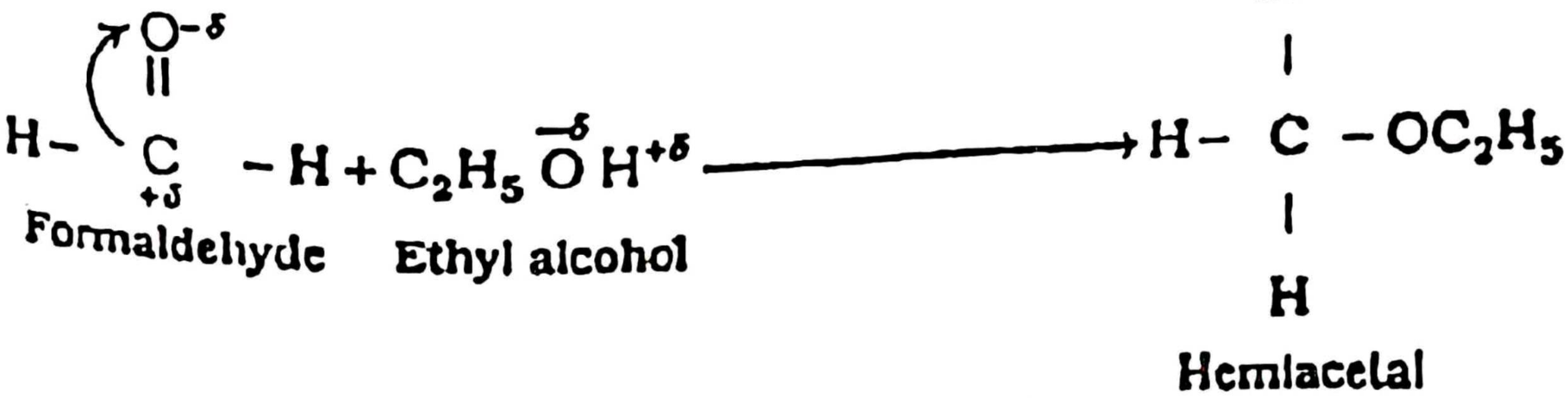
6. Write the equation for the nucleophilic addition reaction if formaldehyde treated with
   i. Hydrogen cyanide ii. Primary alcohol
   iii. Methyl magnesium bromide iv. Ammonia

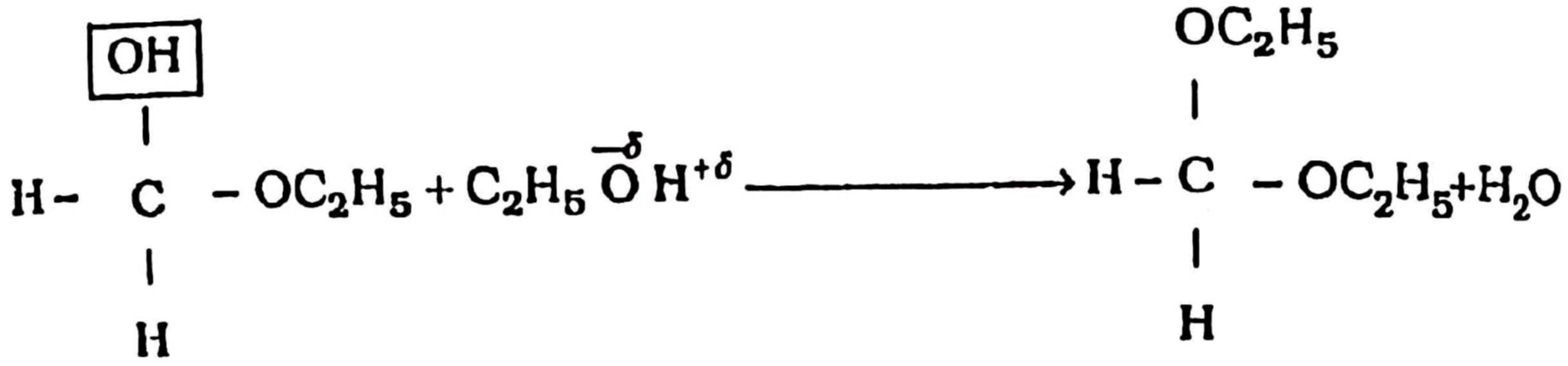
(i)



(ii)

...tal is formed.





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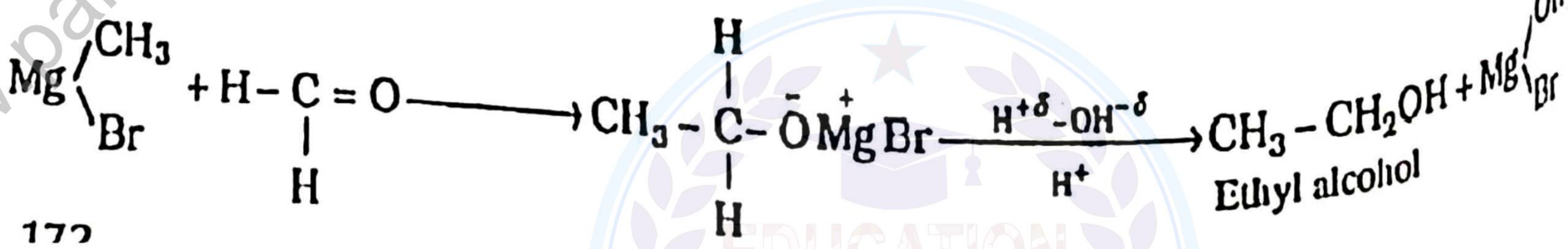

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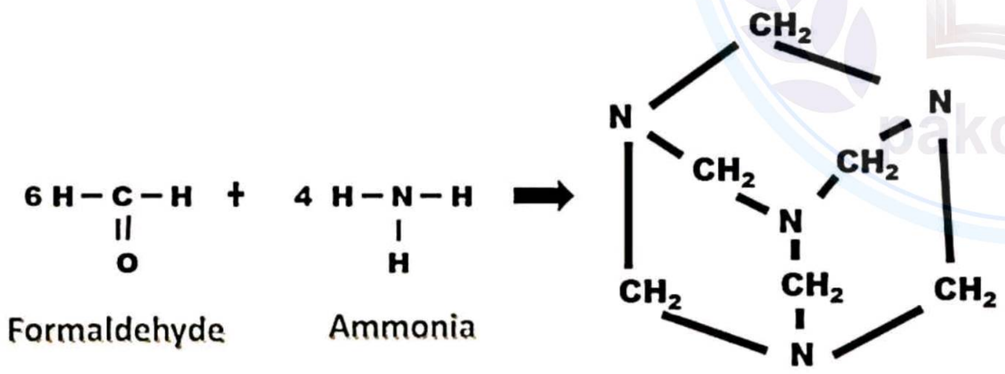

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7. Explain the factors that influence the reactivity of carbonyl compounds towards nucleophilic addition reaction.

ALREADY DISCUSSED ABOVE