Chapter#12

Aldehydes and Ketones

1. Describe preparation of formalin from methanol on commercial scale.

Ans: **Industrial (Commercial) Method:**

Formaldehyde (Formalin) is manufactured commercially by passing a mixture ofmethanol vapours and air over iron oxide-molybdenum oxide or silver catalyst at 500^{o}C.

$$2CH_3OH + O_2 \xrightarrow[500^{o}C]{FeO,Mo_2O_3} 2H-\overset{\overset{O}{\|}}{C}-H + 2H_2O$$

2. Explain one method of formation of formaldehyde from methyl alcohol.

Ans: Formaldehyde is prepared in the laboratory by passing a mixture of methyl alcohol vapours and air over platinized asbestos or copper or silver catalyst at 300 ^{o}C.

$$2CH_3OH + O_2 \xrightarrow[300^{o}C]{\text{Pt-asbestos}} 2H-\overset{\overset{O}{\|}}{C}-H + 2H_2O$$

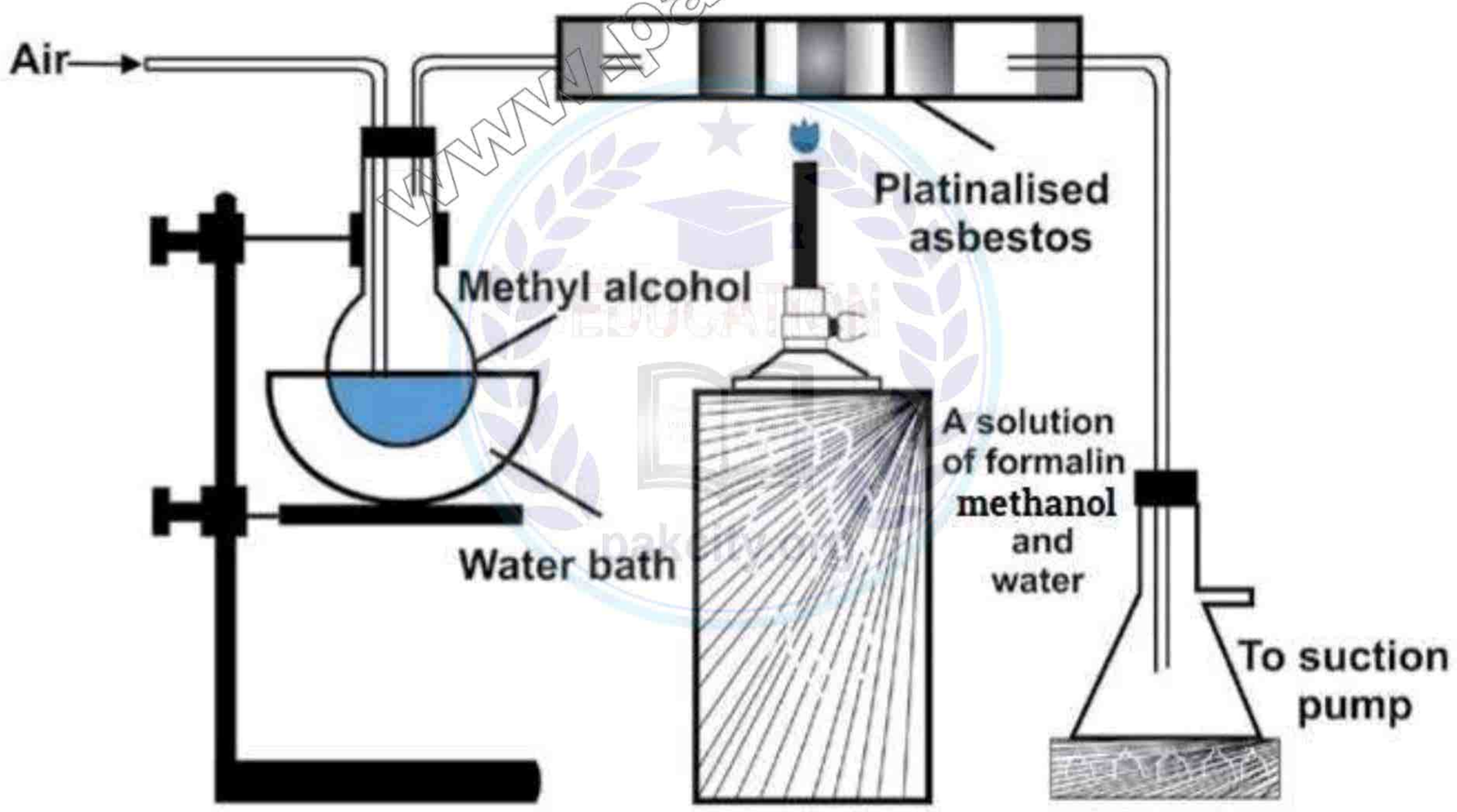
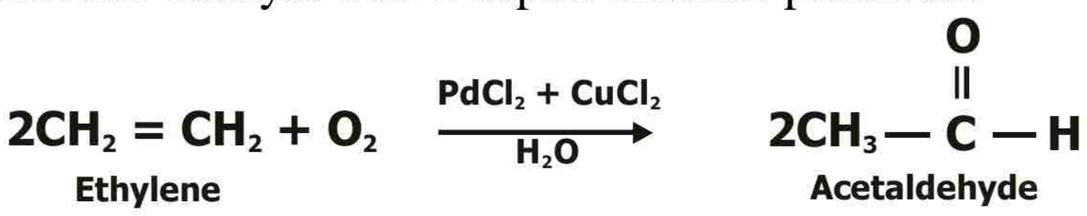


Fig. Preparation of Formaldehyde (formalin)

3. Write a method for the commercial preparation of acetaldehyde?

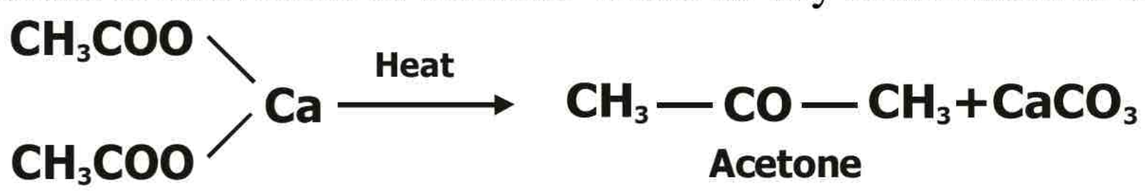
Ans: **Industrial Method:**

Acetaldehyde is prepared industrially by oxidation of ethylene in air using palladiumchloride catalyst with a cupric chloride promoter.



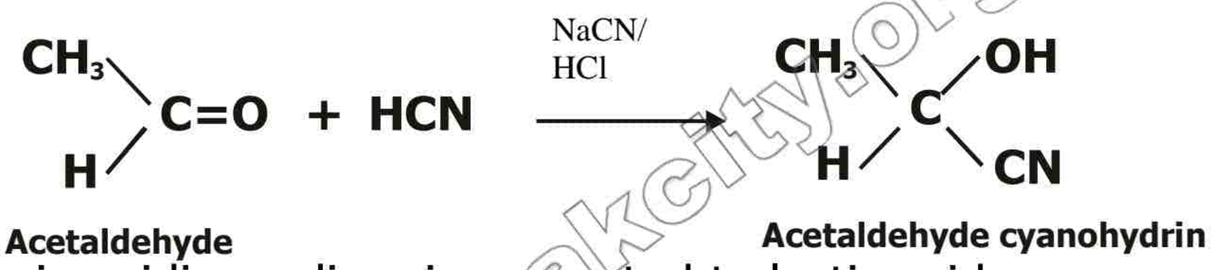
4. Convert calcium acetate to acetone.

Ans: Calcium acetate is converted to acetone when its dry distillation is done.

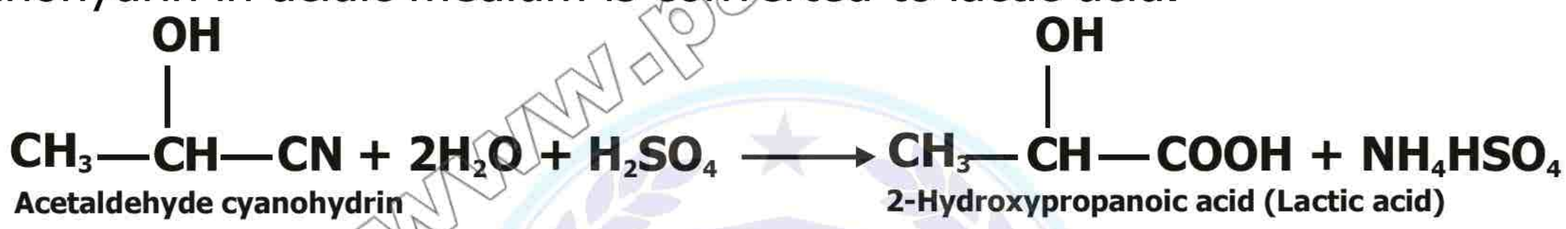


5. Convert acetaldehyde into lactic acid.

Ans: **Acetaldehyde is reacted with hydrogen cyanide to produce acetaldehyde cyanohydrin.**



Cyanohydrin in acidic medium is converted to lactic acid.



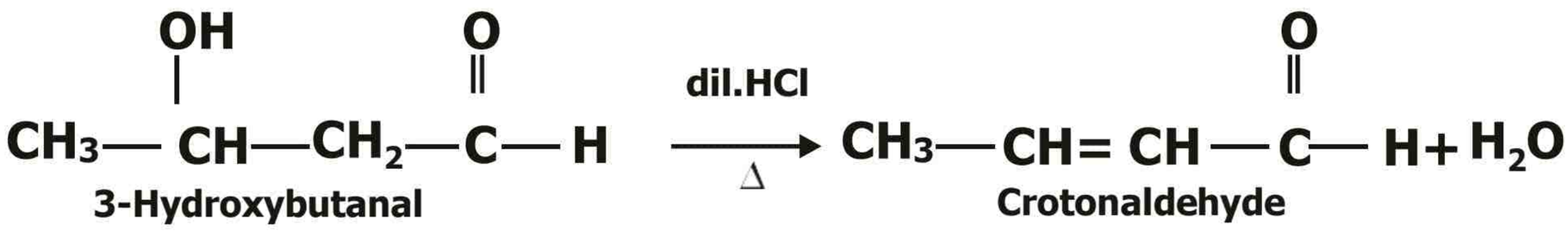
6. For Aldol condensation the presence of α-hydrogen is must in aldehydes and ketones. Give reasons.

Ans: Aldol condensation proceeds through the formation of carbanion in the first step. This ion is produced when the acidic hydrogen at the α-carbon is removed by the base (OH^-). In the absence of α-hydrogen, carbanion cannot be produced, so aldol condensation cannot take place.

7. How is crotonaldehyde obtained from Aldol?

Ans: **Conversion of Aldol to Croton aldehyde:**

The aldol undergoes dehydration on heating in the presence of dilute acid to form α,β- unsaturated carbonyl compound. A carbon-carbon double bond is formed between the α-and β-carbon atoms.



8. What are disproportionation reactions?

Ans: It is a disproportionation (self oxidation-reduction) reaction. The molecules being oxidized and reduced are the same chemical species.

Example:

9. Justify that Cannizaro's reaction is a self-redox reaction.

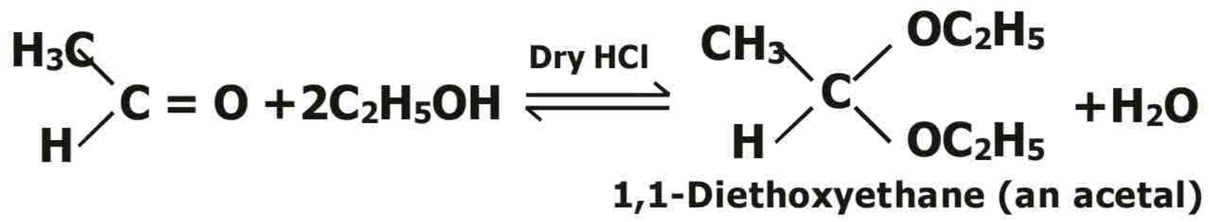
Ans: In Cannizaro's reaction, one of the molecules of aldehyde is oxidized and the other is reduced. The oxidation yields carboxylic acid and reduction alcohol. (Mechanism already discussed in exercise questions section given above. Benedict's solution are some examples of mild oxidizing agents.

10. **Convert formaldehyde to meta-formaldehyde?**

Ans: Formaldehyde polymerizes in the presence of dil. H_2SO_4 to give Meta formaldehyde asshown below.

11. What is the importance of converting aldehyde to Acetal?

Ans: Aldehydes combine with alcohols in the presence of hydrogen chloride gas to form acetalas shown below.

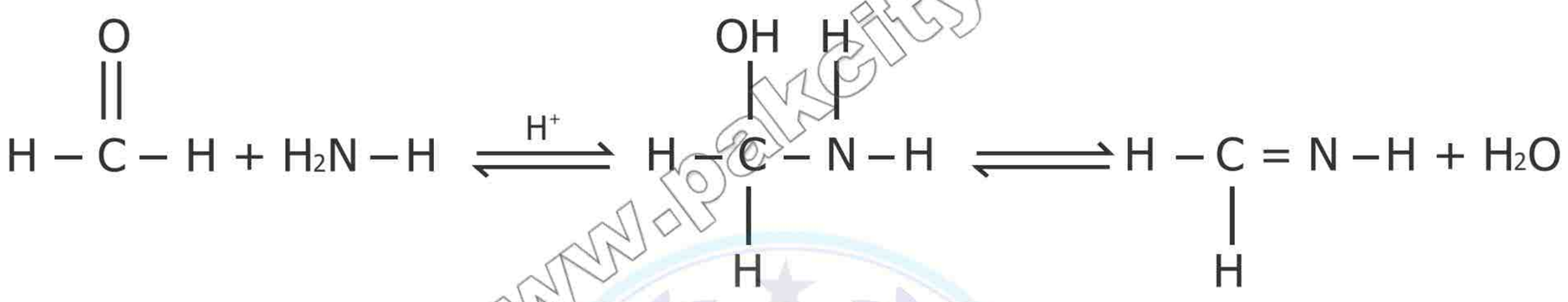


Importance of reaction:

The reaction may be used to protect the aldehyde group against alkaline oxidizing agents. To regenerate Aldehyde, the Acetal is hydrolyzed in the presence of an acid.

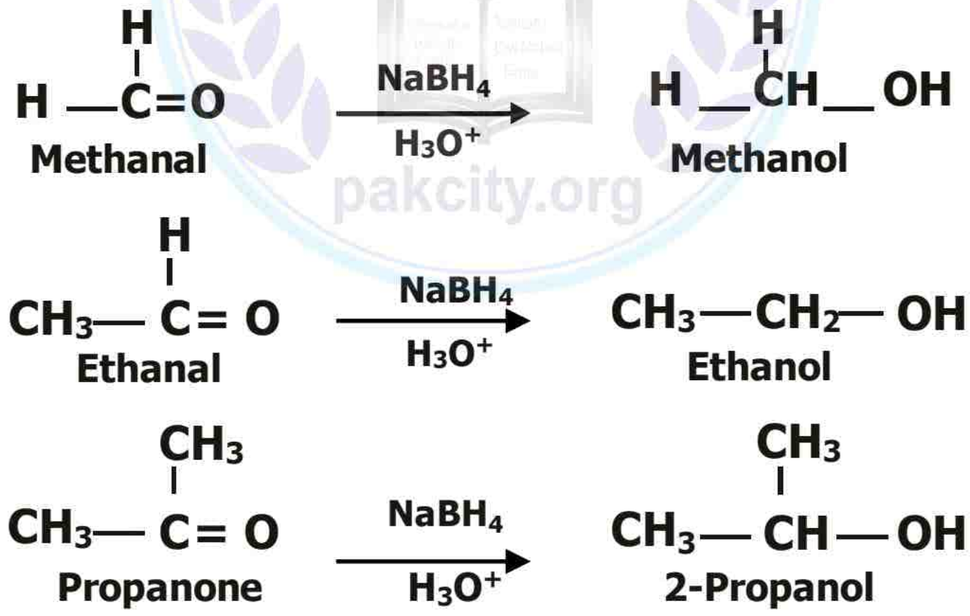
12. Describe reaction of aldehyde with ammonia?

Ans: Aldehyde and Ketones react with ammonia (H-NH_2) to form compounds containing the group -C = N and water. The reaction is known as condensation reaction or elimination reaction because water is lost after addition occurs. This reaction is acid catalyzed.



13. How aldehydes and Ketones are reduced to alcohols?

Ans: Aldehydes and ketones are reduced to alcohols with sodium borohydride ($NaBH_4$) in acidicmedium.



14. Write the names of those weak oxidizing agents which can oxidize aldehydes butnot ketones.

Ans: Some examples of such oxidizing agents are as follows

(i) Fehling's solution (an alkaline solution containing a cupric tartrate complex ion)
(ii) Benedict's solution (an alkaline solution containing a cupric citrate complex ion)
(iii) Tollen's reagent (ammonical silver nitrate solution)

15. Why the oxidation of Ketones is difficult?

Ans: Ketones do not undergo oxidation easily because they require breaking of strong carbon– carbon bond. They give no reaction with mild oxidizing agents. They are only oxidized by strong oxidizing agents such as $K_2Cr_2O_7/H_2SO_4$, $KMnO_4/H_2SO_4$, and conc. HNO_3

16. What are the factors which make aldehydes more reactive than ketones?

Ans: The following two factors account for this:

i) The presence of hydrogen atom with the carbonyl group in aldehyde decreases steric hindrance around carbonyl carbon. In ketones there is more steric hindrance.
ii) In ketones the two alkyl groups (electron donating groups) decrease the electrophilic character of carbonyl carbon atom to a great extent while one alkyl group in aldehyde does not decrease the electrophilic character of carbonyl carbon atom to that extent.

17. How aldehydes are identified by Tollen's test?

OR

Tollen's test is also called silver mirror test. Justify it.

Ans: **Tollen's Test [Silver Mirror Test]:**

Aldehydes form silver mirror with Tollens' reagent (ammonical silver nitrate solution). Add Tollens' reagent to an aldehyde solution in a test tube and warm. A silver mirror is formed on the inside of the test tube.

$$AgNO_3 + 3NH_4OH \longrightarrow [Ag(NH_3)_2]OH + NH_4NO_3 + 2H_2O$$

$$R\text{-}CHO + 2[Ag(NH_3)_2]OH \longrightarrow \underset{\text{Silver mirror}}{R\text{-}COONH_4} + 2Ag + 2NH_3 + H_2O$$

18. Give examples of mild oxidizing agents?

Ans: The reagents or compounds which can only oxidize aldehydes and not the ketones arecalled mild oxidizing agents such as Tollen's reagent, Fehling's solution etc.

19. Fehling's solution reacts with aldehydes to give red ppt. justify it.

Ans: Fehling's solution is a mixture of $Cu(OH)_2$, NaOH and tartaric acid. It reduces aldehydeand produces brick red ppt of Cu_2O on heating.

$$H-\underset{\underset{O}{\|}}{C}-H + 2Cu(OH)_2 + NaOH \xrightarrow{\text{Tartaric acid}} \underset{\text{Sodium salt of acid}}{R-\underset{\underset{O}{\|}}{C}-ONa} + \underset{\text{Red ppt.}}{Cu_2O\downarrow} + 3H_2O$$

20. How is acetaldehyde distinguished from formaldehyde?

Ans:

Acetaldehyde (Ethanal)	Formaldehyde (Methanal)
Ethanal produces yellow ppt of Iodoform (CHI_3) with NaOH and I_2. **$CH_3\text{-}CHO + 3I_2 + 4NaOH \rightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$**	Methanal does not produce Iodoform with NaOH and I_2. **$H\text{-}CHO + I_2 + NaOH \rightarrow$ No reaction**

21. How Iodoform is prepared from ethanol and acetaldehyde?

Ans: **Preparation of iodoform from ethanol and acetaldehyde:**

Heating ethanol or acetaldehyde with NaOH and solid iodine gives Iodoform as follows: -

$$C_2H_5OH + 4I_2 + 6NaOH \rightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$$
$$CH_3\text{-}CHO + 3I_2 + 4NaOH \rightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$$

22. Give uses of formaldehyde (Any two or four can be asked)

Ans: **Uses of formaldehyde:**

(i) It is used in the manufacture of resins like urea-formaldehyde and plastics such as bakelite.
(ii) It is used in the manufacture of dyes such as indigo, para-rosaniline, etc.
(iii) Its 40% aqueous solution called formalin is used as an antiseptic, a disinfectant, a germicide, a fungicide and for preserving animal specimens and sterlising surgical instruments.
(iv) It is used as a decolourising agent in vat dyeing.
(v) It is used in the silvering of mirrors.
(vi) It is used in making medicine urotropine used as a urinary antiseptic.
(vii) It is used in making formamint (formaldehyde + lactose) used as throat lozenges.
(viii) It is used in the processing of anti-polio vaccine.

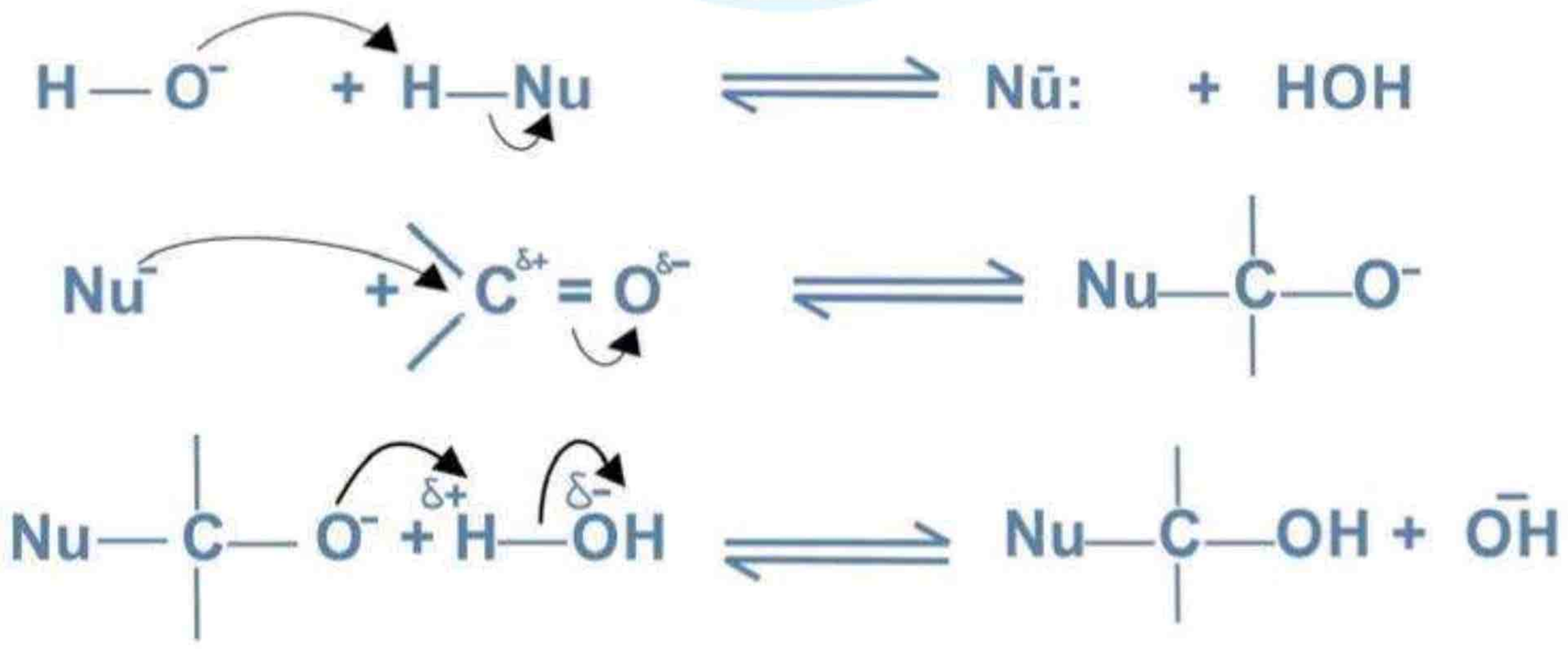
23. Write uses of acetaldehyde (Any two or four can be asked)

Ans: **Uses of acetaldehyde:**

1. It is used in the production of acetic acid, acetic anhydride, n-butanol, ethanol, 2-ethyl-1-hexanol, vinyl acetate, paraldehyde, ethylacetate, etc.
2. It is used to make acetaldehyde ammonia used as a rubber-accelerator.
3. It is used to make chloral hydrate, ethanol trimer and tetramer. Chloral hydrate and ethanol trimer are both used as hypnotic drugs whereas ethanol tetramer is used as a slug poison.
4. It is used as an antiseptic inhalent in nasal infections.
5. It is used in silvering of mirrors.
6. It is used to make phenolic resins and synthetic drugs.

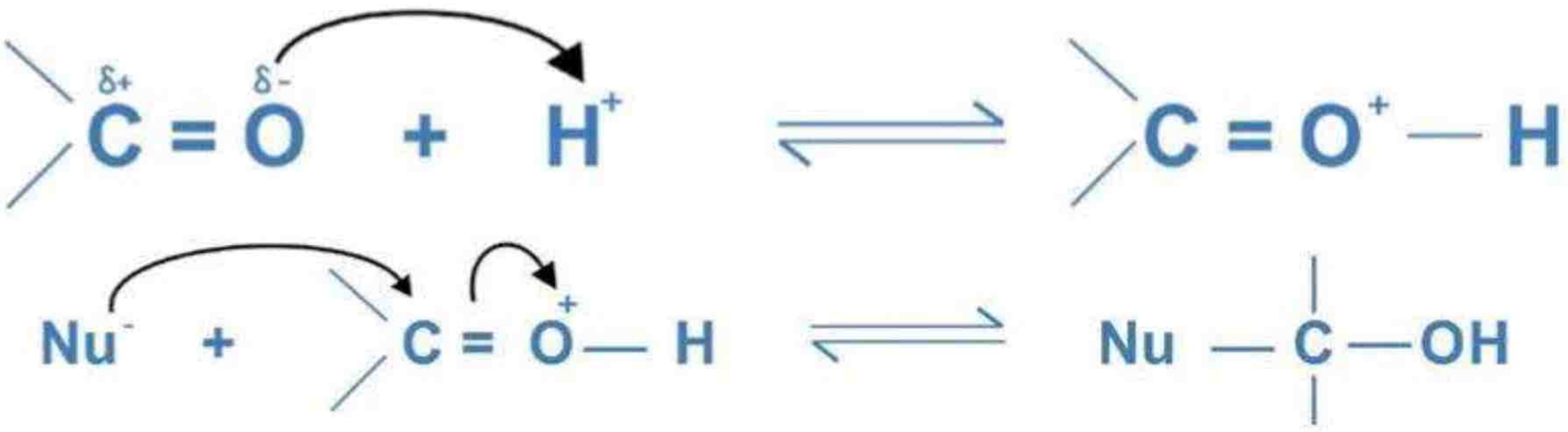
24. Describe briefly the base-catalyzed mechanism of nucleophilic addition to a carbonyl compound.

Ans:



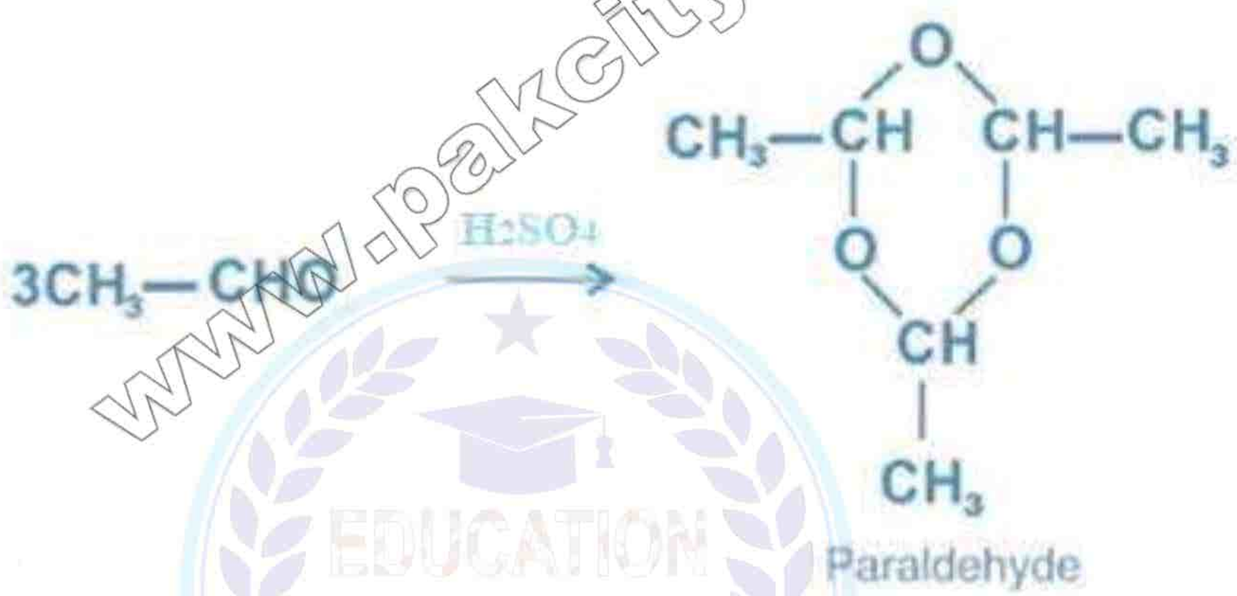
25. Describe briefly the acid-catalyzed mechanism of nucleophilic addition to a carbonyl compound.

Ans:



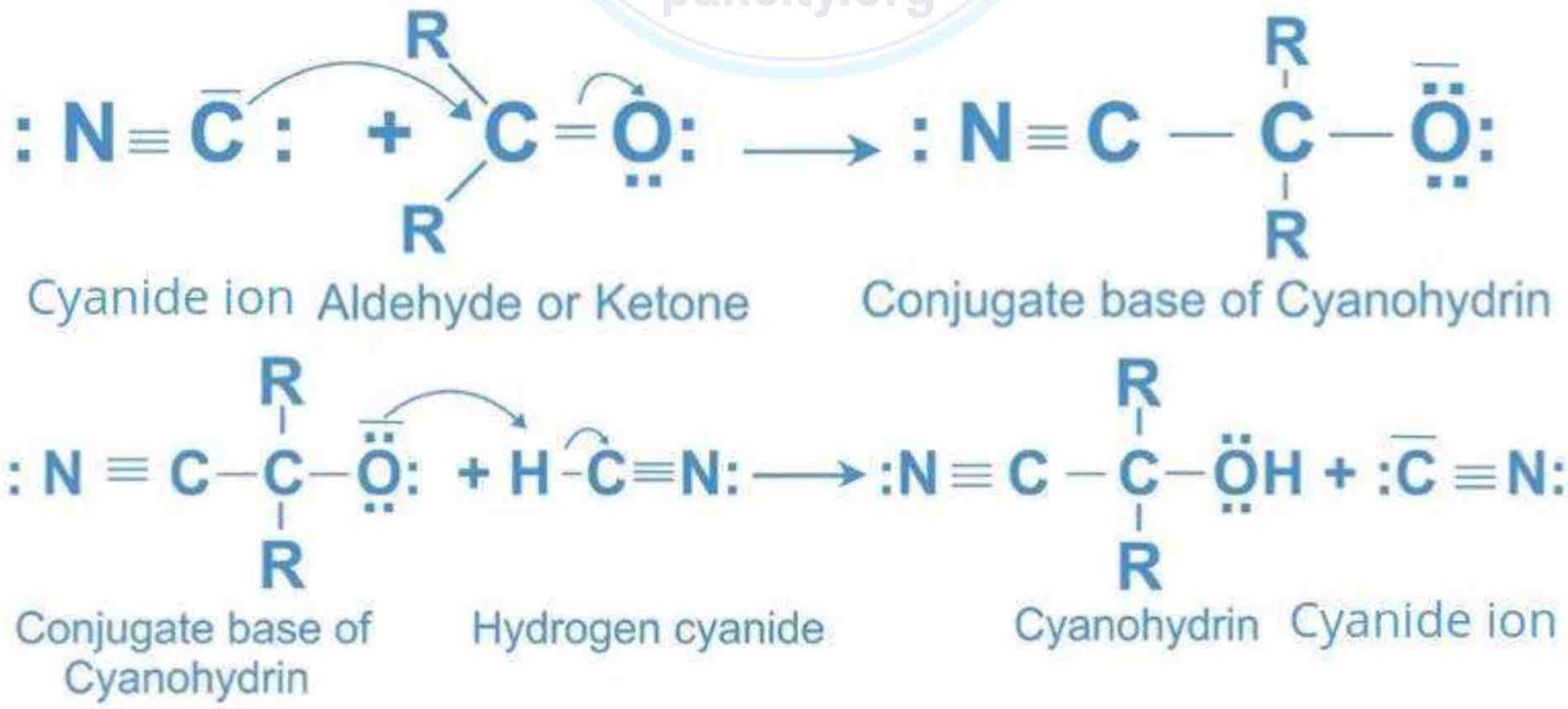
***26.* Convert acetaldehyde to paraldehyde.**

Ans: Acetaldehyde polymerizes in the presence of dil.H_2SO_4 to give paraldehyde as shownbelow:



***27.* Give the mechanism of addition of HCN to aldehyde or ketone.**

Ans:



28. Describe preparation of acetaldehyde from ethanol in laboratory.

Ans: Acetaldehyde is prepared in the laboratory by the oxidation of ethyl alcohol with acidified sodium dichromate solution. A mixture of ethyl alcohol and sodium dichromate solution is run into boiling dilute sulphuric acid. Immediately a vigorous reaction takes place and the acetaldehyde formed in liquid state is immediately distilled off. This prevents the oxidation of acetaldyde to acetic acid. Ethyl alcohol remains in solution until it is oxidized. Pure acetaldehydeis obtained by redistillation.

$$CH_3CH_2OH + [O] \xrightarrow[\Delta]{Na_2Cr_2O_7 + H_2SO_4} CH_3CHO + H_2O$$

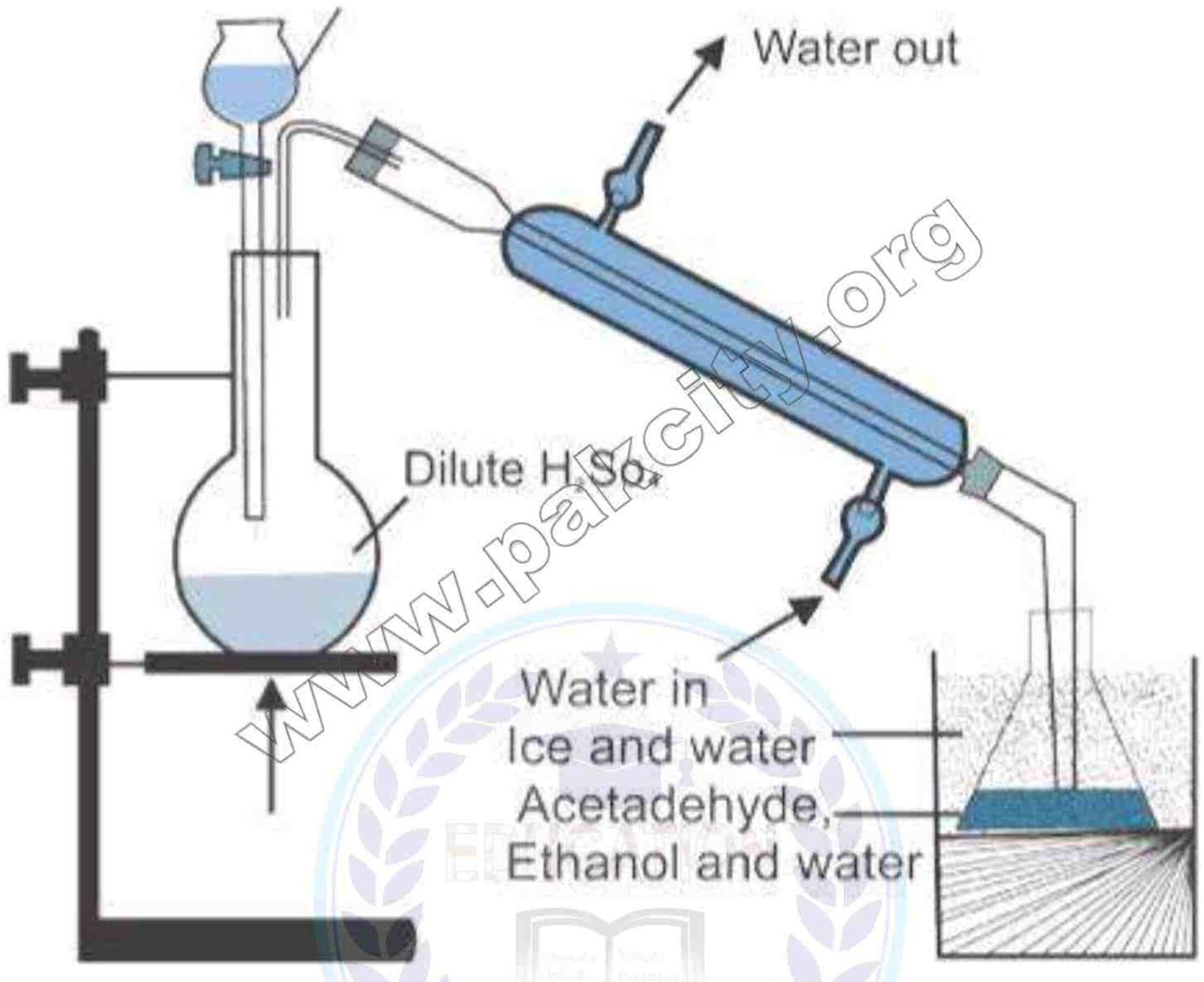
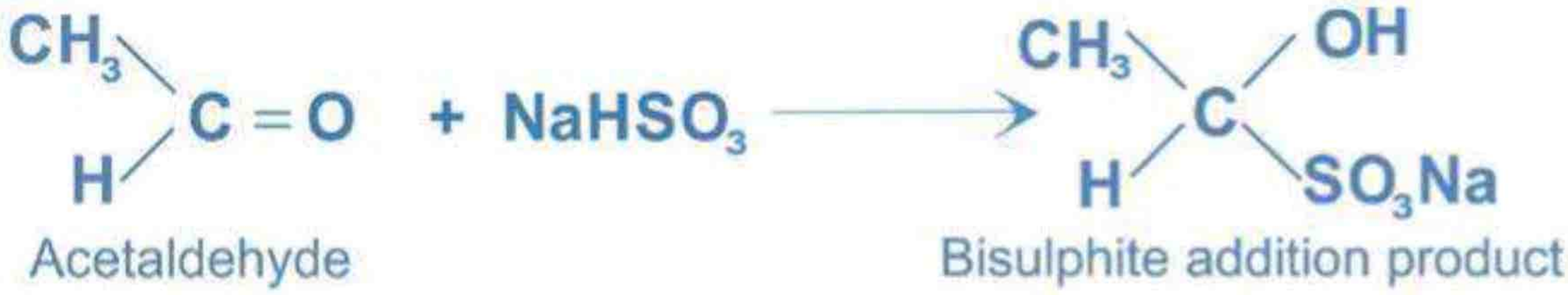


Fig. Preparation of Acetaldehyde

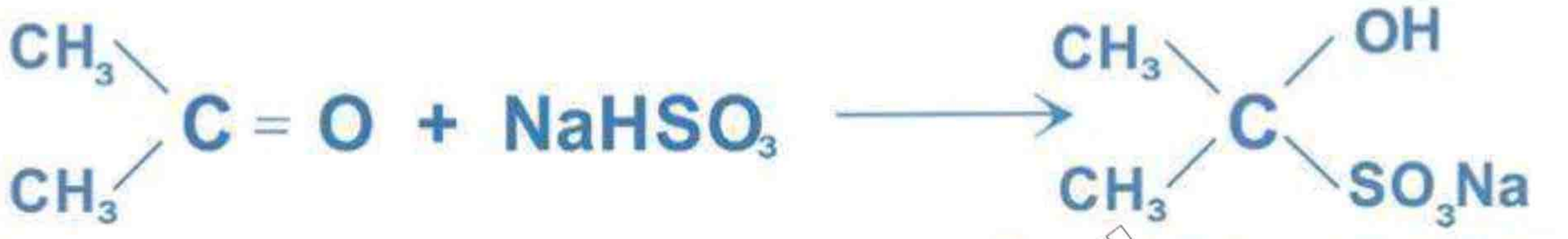
29. How aldehydes and ketones react with $NaHSO_3$?

Ans: Aldehydes and small methyl ketones react with a saturated aqueous solution of sodiumbisulphite to form a crystalline white precipitate of sodium bisulphite adduct.

Formaldehyde Bisulphite addition product



Acetaldehyde Bisulphite addition product

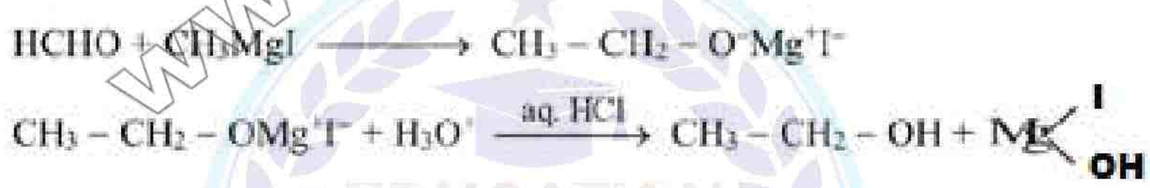


Acetone Bisulphite addition product

30. How does formaldehyde react with the following reagents?

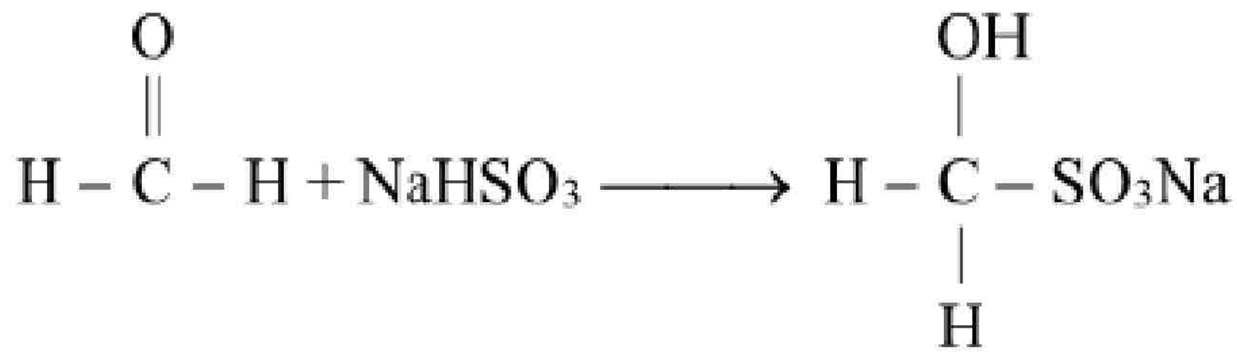
Ans:

(i) CH_3MgI



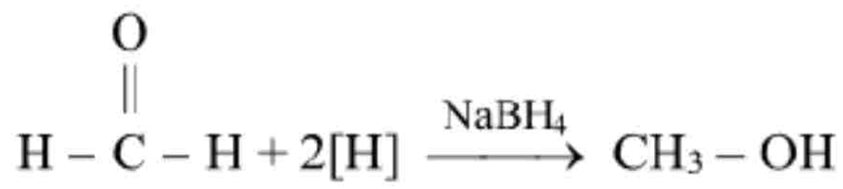
(ii) HCN

(iii) $NaHSO_3$



(iv) NaOH

(v) Hydrogen



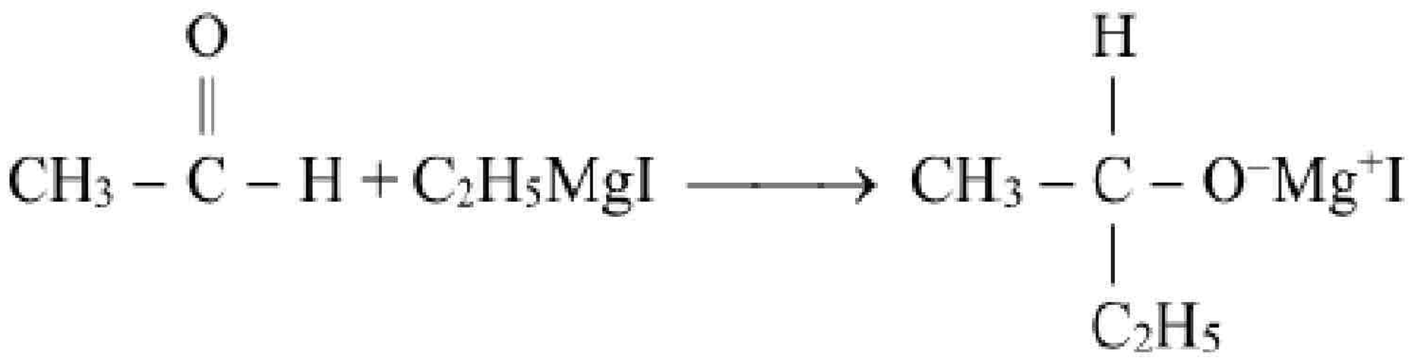
(vi) Tollen's Reagent

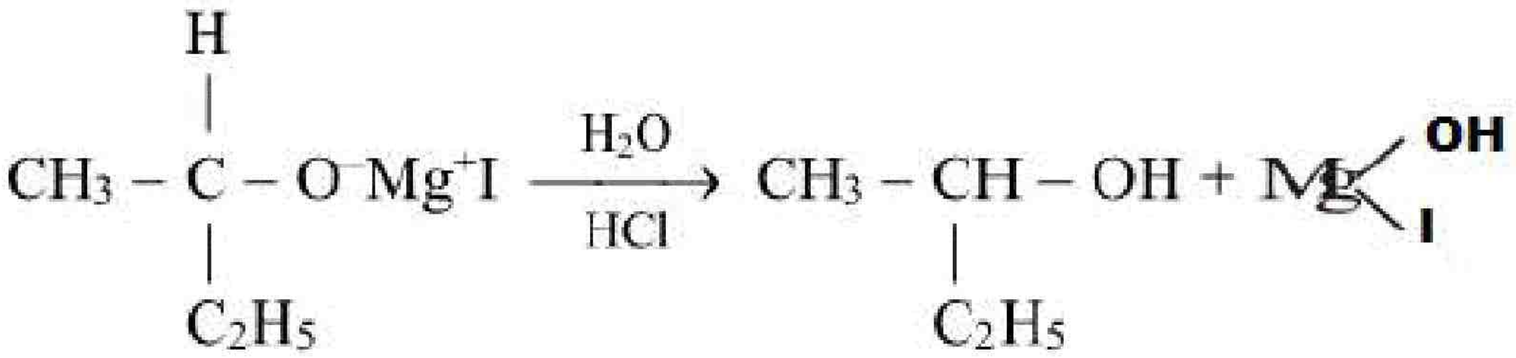
(vii) Fehling's Reagent

31. How does acetaldehyde react with following?

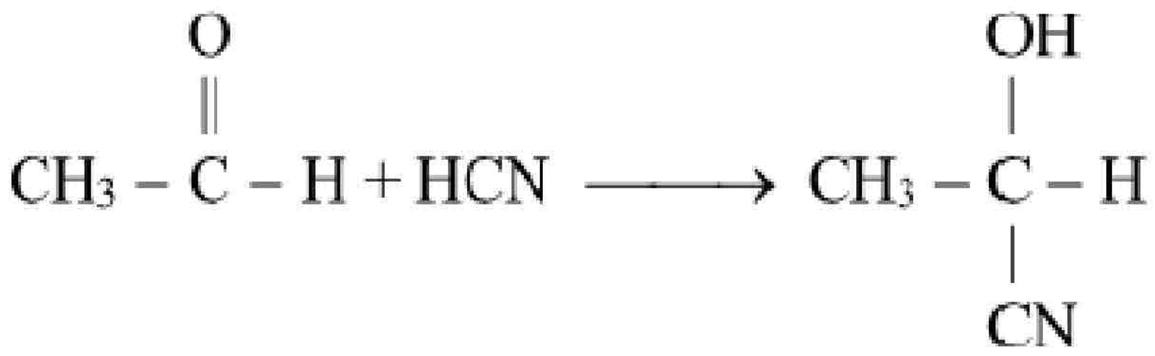
Ans:

(i) C_2H_5MgI





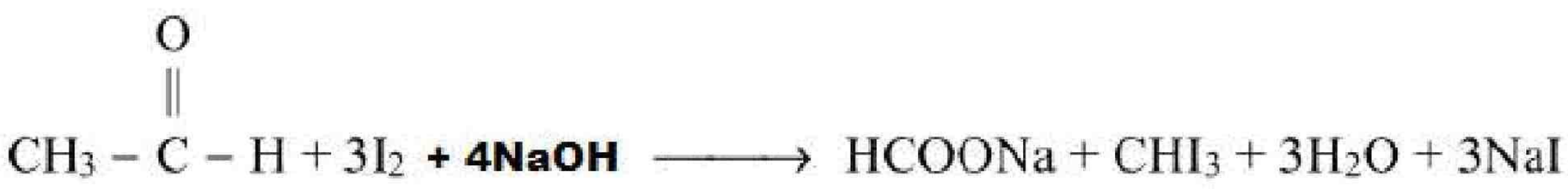
(ii) HCN



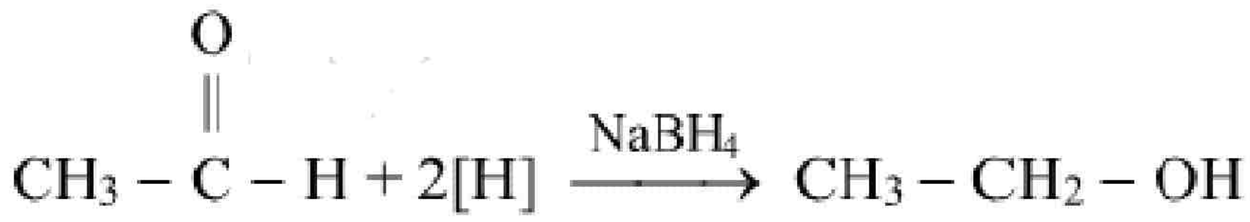
(iii) $NaHSO_3$

(iv) dil. NaOH

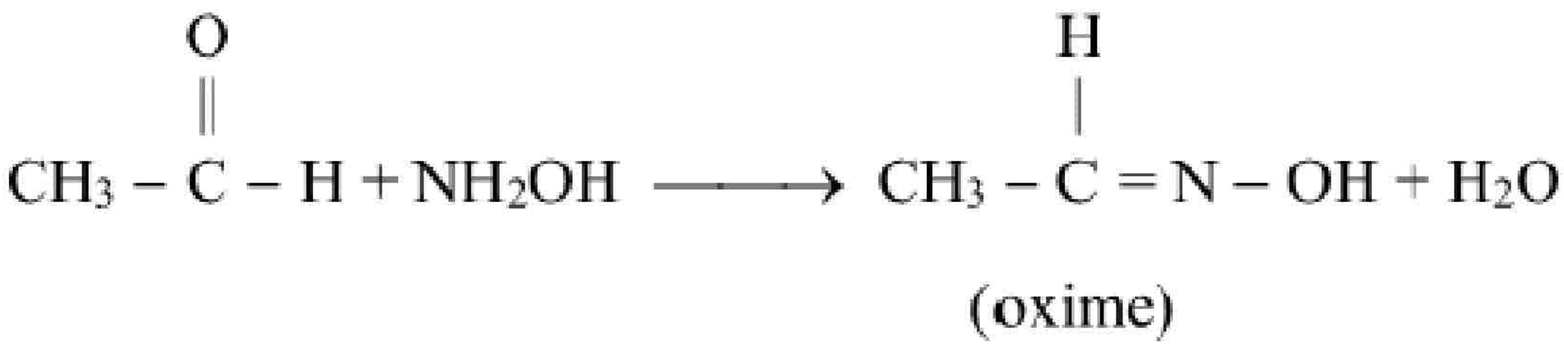
(v) I_2/NaOH



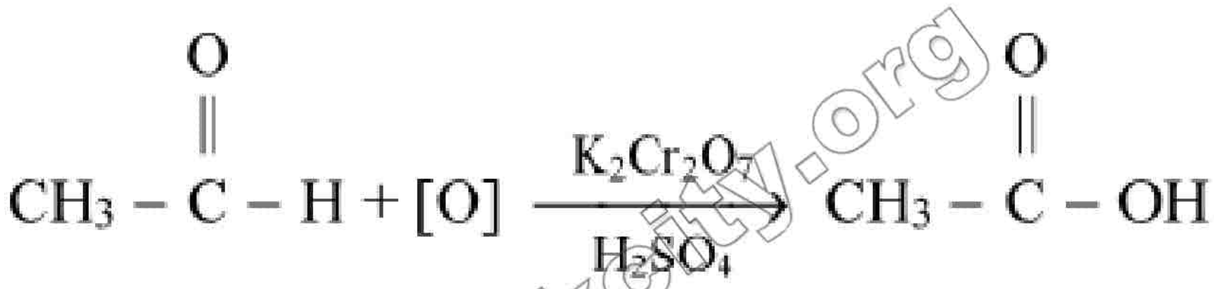
(vi) $NaBH_4/H_2O$



(vii) NH_2OH



(viii) $K_2Cr_2O_7/H_2SO_4$

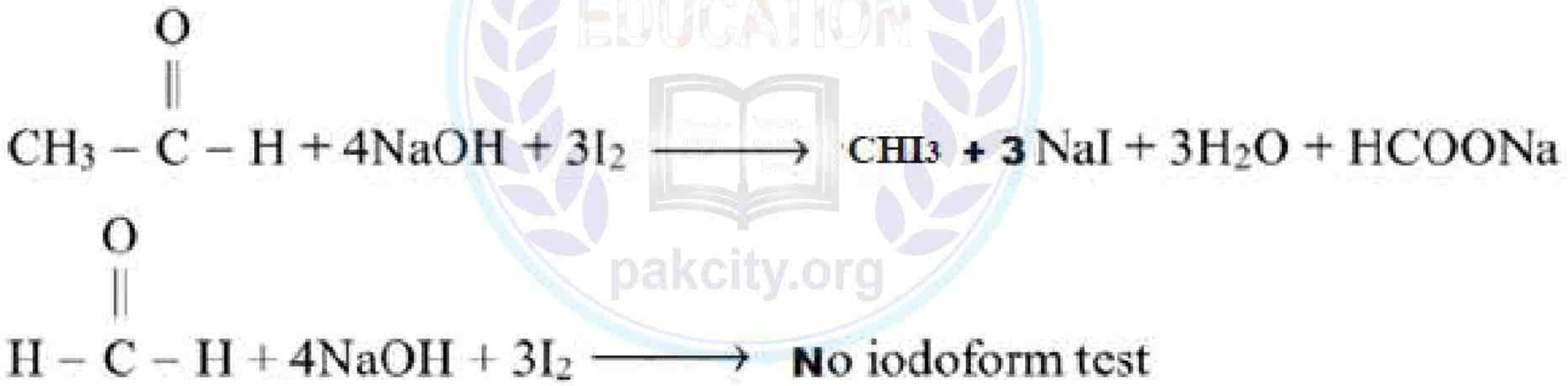


32. How will you distinguish between:

Ans:

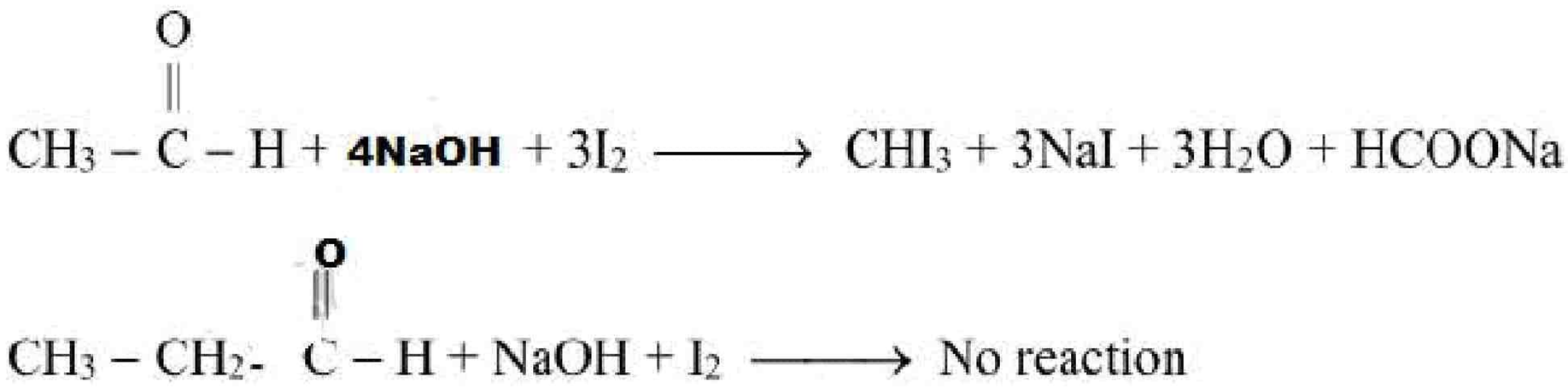
(i) Methanal and Ethanal

Both can be distinguished by iodoform test.



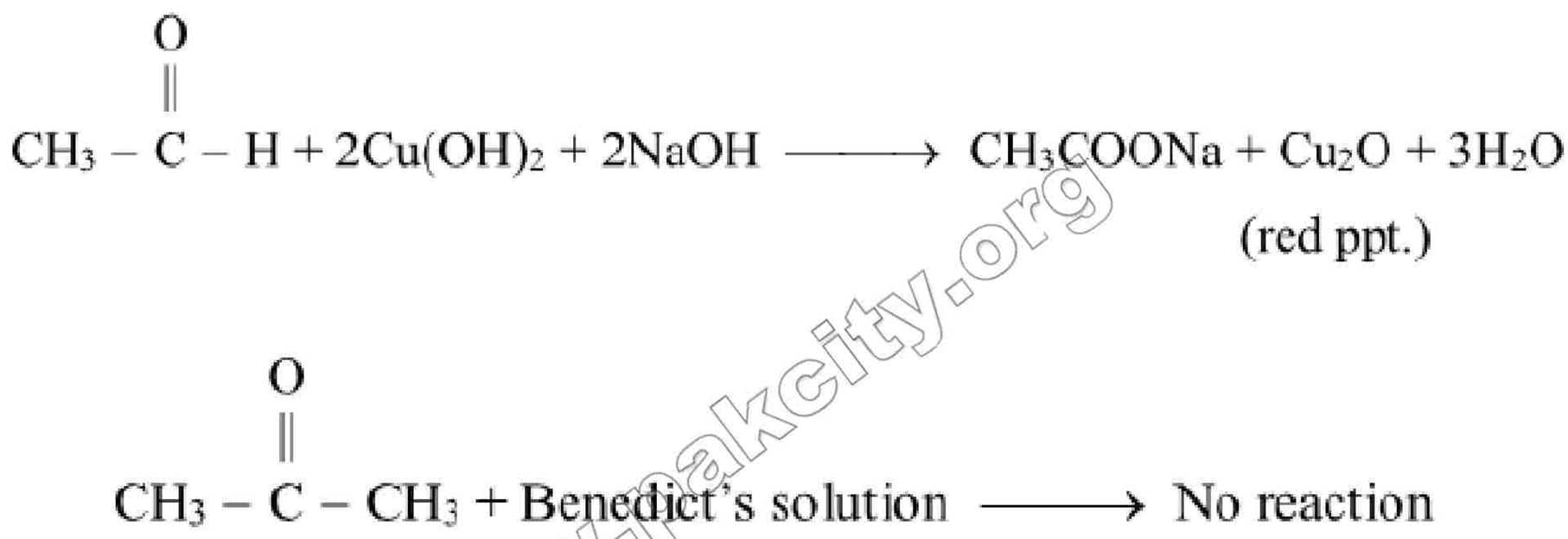
(ii) Ethanal and Propanal

Both can be distinguished by iodoform test.



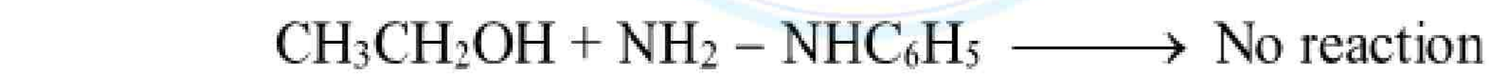
(iii) Ethanal and Propanone

Both can be distinguished by mild oxidizing agent, e.g., Benedict's, Fehling's.



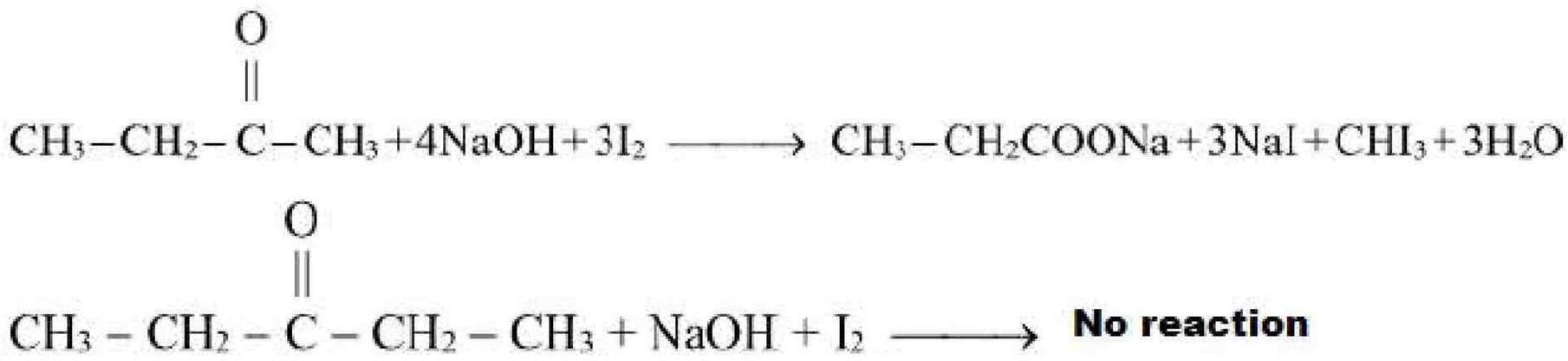
(iv) Acetone and Ethyl alcohol

Both can be distinguished by reacting with phenylhydrazine



(v) Butanone and 3-pentanone

Both can be distinguished by iodoform test



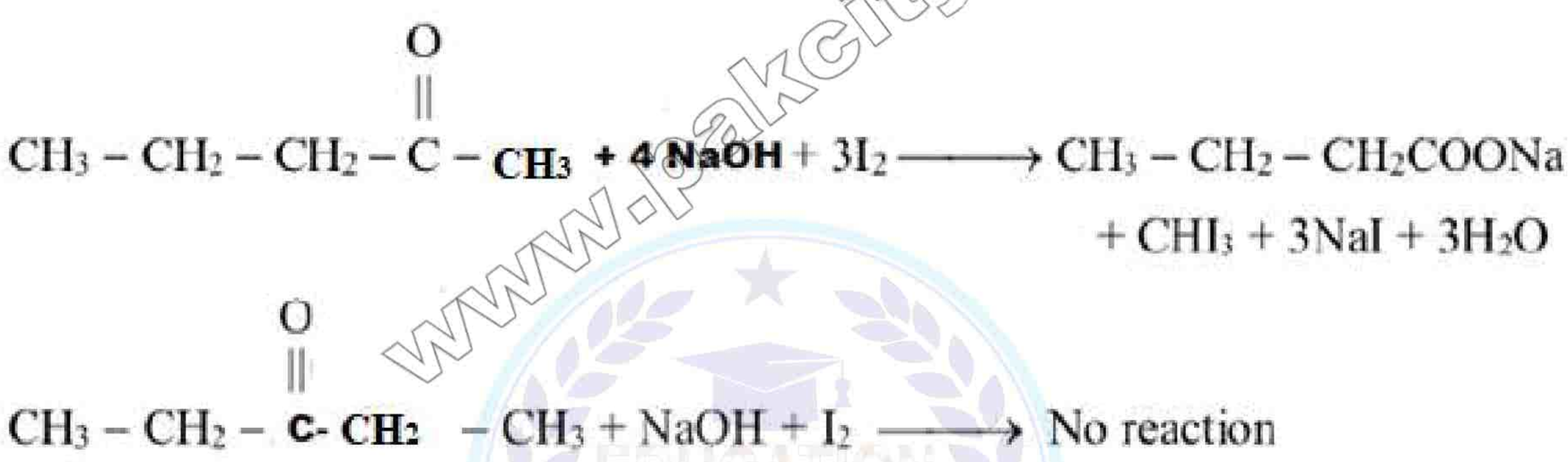
(vi) Acetaldehyde and Benzaldehyde

Acetaldehyde gives iodoform test whereas benzaldehyde gives no iodoform test

Benzaldehyde gives cannizzaro's reaction while acetaldehyde gives aldol product

(vii) 2-pentanone and 3-pentanone

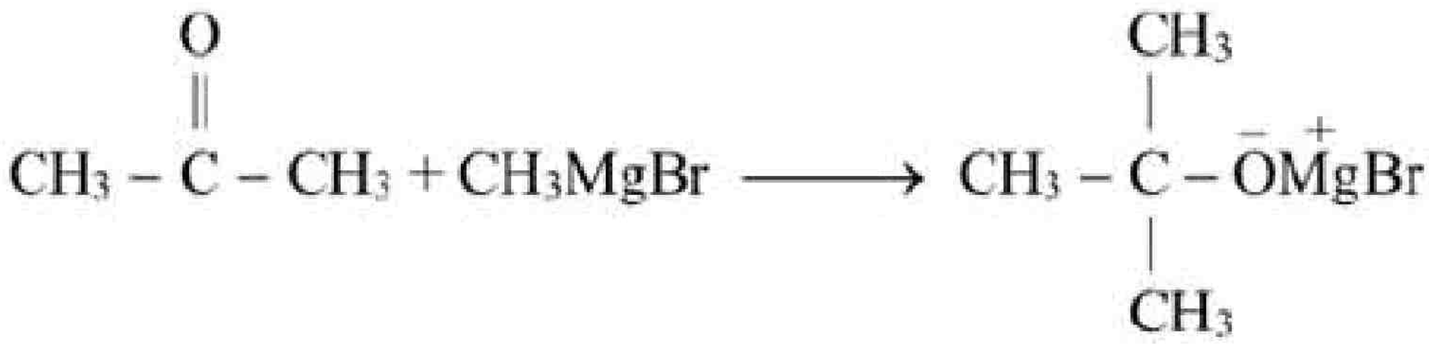
Both can be distinguished by iodoform test

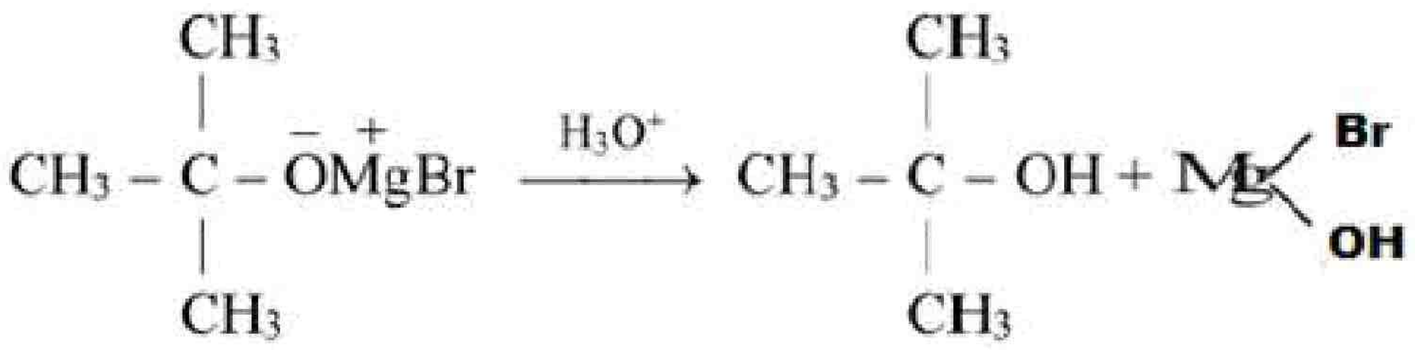


33. How will you bring about the following conversions:

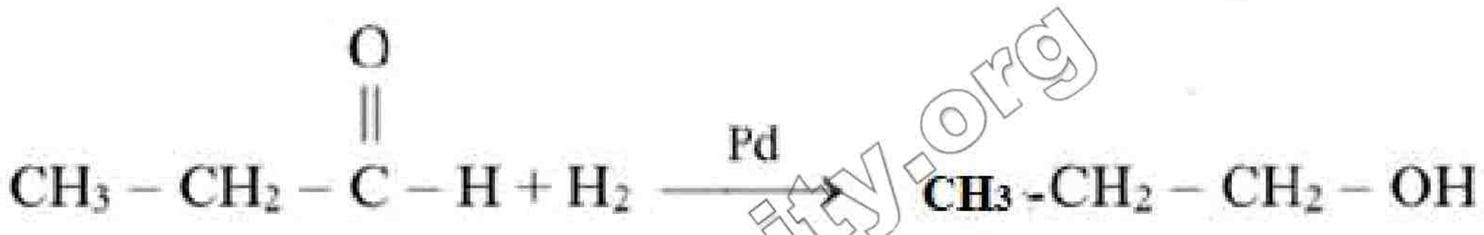
Ans:

(i) Acetone ⟶ t-Butyl alcohol

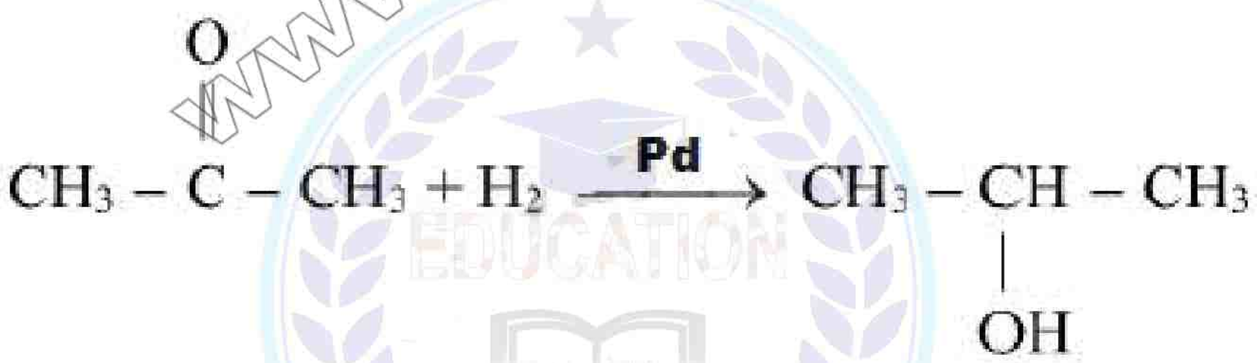




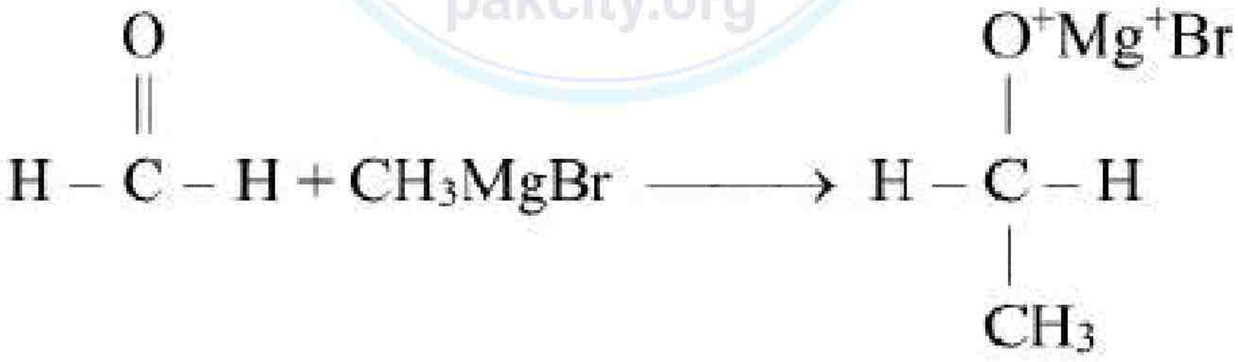
(ii) Propanal ⟶ 1-propanol:

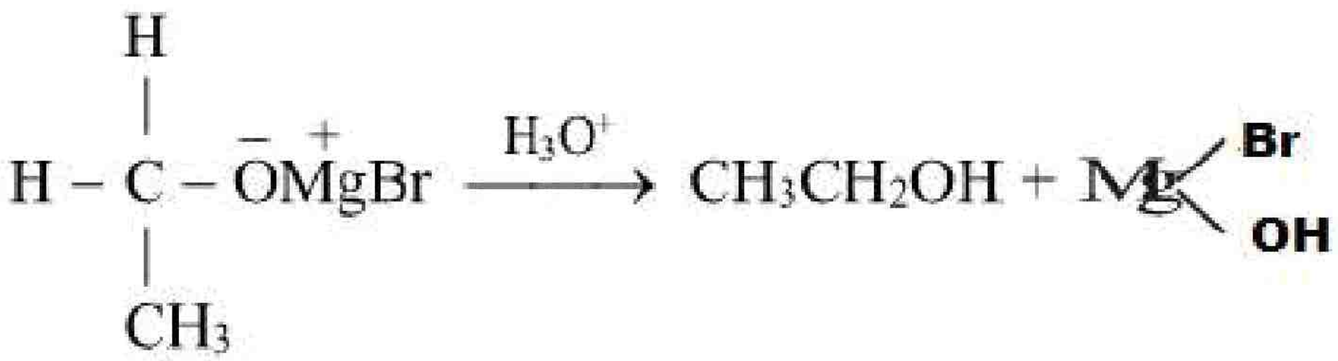


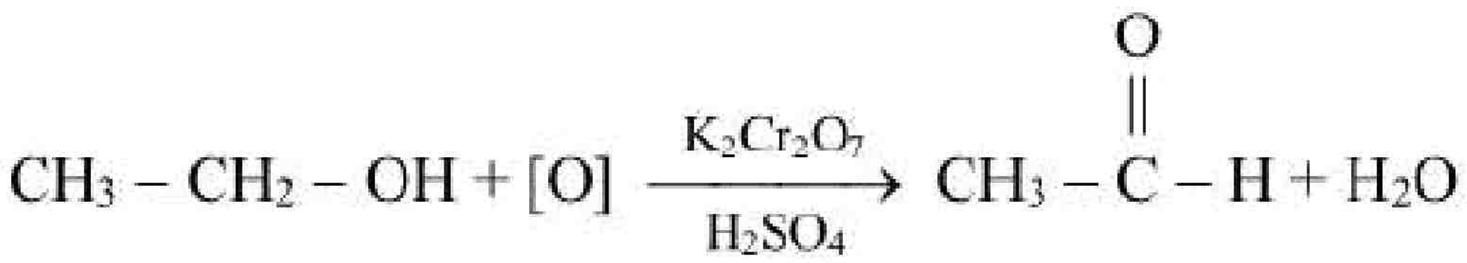
(iii) Propanone ⟶ 2-propanol



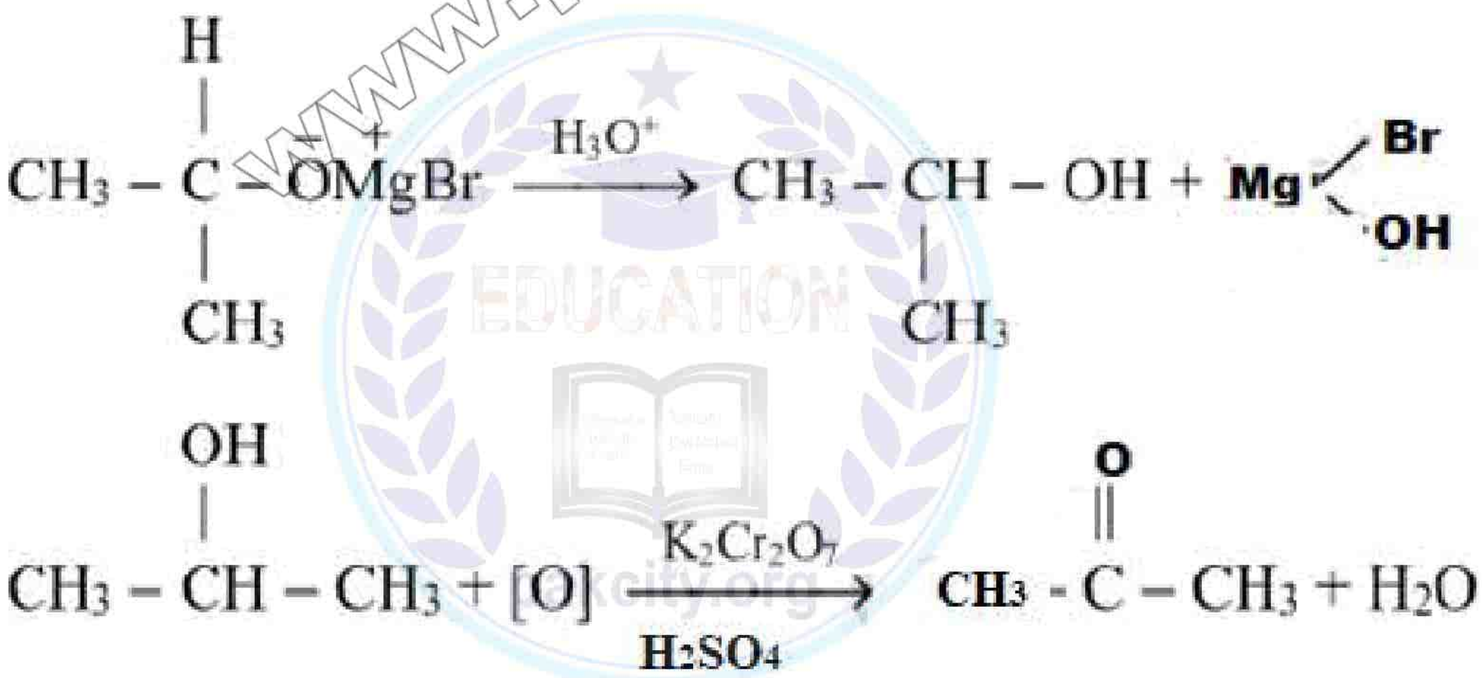
(iv) Methanal ⟶ Ethanal:



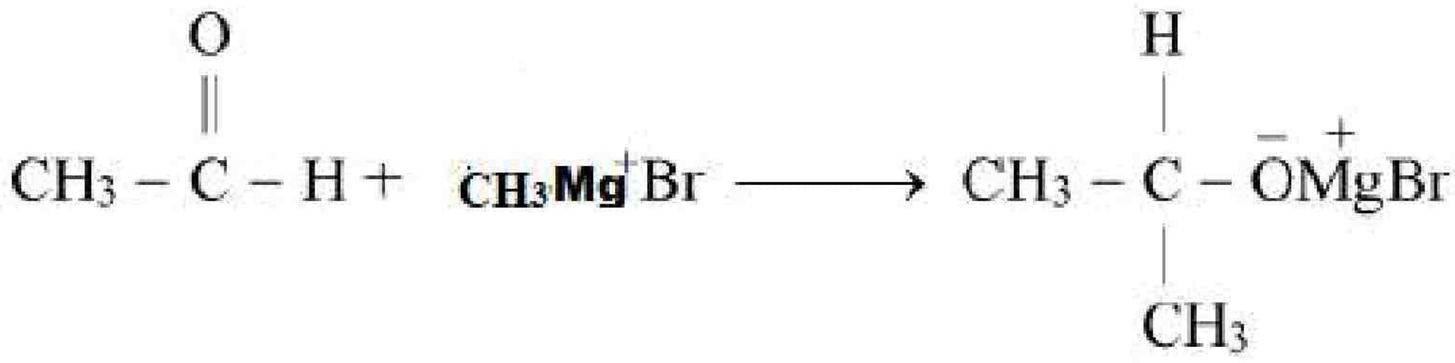


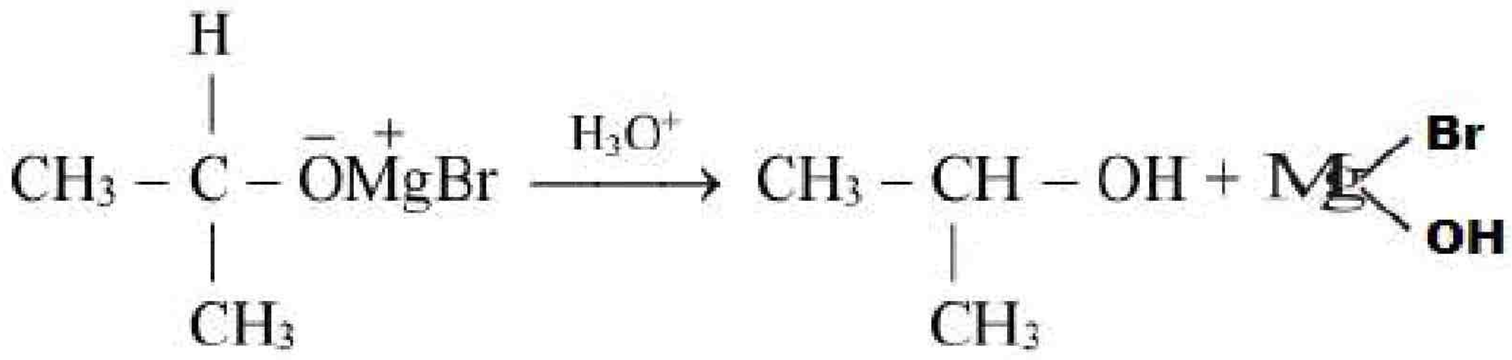


(v) Ethanal ⟶ propanone:



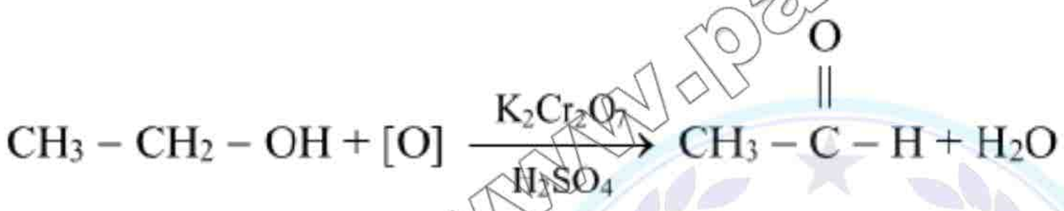
(vi) Ethanal ⟶ 2-propanol





(vii) Ethene ⟶ Ethanal:

$$CH_2 = CH_2 + H_2O \longrightarrow CH_3 - CH_2 - OH$$



(viii) Ethanal ⟶ Ethanol:

(ix) Ethanol ⟶ 2-butanone:

$$CH_3 - CH_2OH + HBr \longrightarrow CH_3CH_2Br + H_2O$$

$$CH_3CH_2Br + Mg \longrightarrow CH_3CH_2MgBr$$

$$CH_3CH_2MgBr + CH_3 - \overset{\overset{O}{\|}}{C} - H \longrightarrow CH_3 - \overset{\overset{OMgBr}{|}}{\underset{\underset{H}{|}}{C}} - CH_2 - CH_3$$

$$CH_3 - \overset{\overset{OMgBr}{|}}{\underset{\underset{H}{|}}{C}} - CH_2 - CH_3 + H_2O \longrightarrow CH_3 - \overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}} - CH_2 - CH_3 + Mg\begin{matrix}Br\\OH\end{matrix}$$

$$CH_3 - \overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}} - CH_2 - CH_3 + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3 - \overset{\overset{O}{\|}}{C} - CH_2 - CH_3 + H_2O$$

(x) Methanol ⟶ Ethanal

$$CH_3OH + [O] \longrightarrow H - \overset{\overset{O}{\|}}{C} - H + H_2O$$

$$H - \overset{\overset{O}{\|}}{C} - H + CH_3MgBr \longrightarrow CH_3 - CH_2 - O^-Mg^+Br$$

$$CH_3 - CH_2OMgBr + H_2O \xrightarrow{H_3O^+} CH_3CH_2OH + Mg\begin{matrix}Br\\OH\end{matrix}$$

$$CH_3CH_2OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3 - \overset{\overset{O}{\|}}{C} - H + H_2O$$

(xi) Ethanal ⟶ Ethanoic Acid:

$$CH_3 - \overset{\overset{O}{\|}}{C} - H + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3 - \overset{\overset{O}{\|}}{C} - OH$$

34. Using ethyne as starting material how would you get acetaldehyde, acetone and ethyl alcohol?

Ans:

(i) Acetaldehyde:

$$CH \equiv CH + H_2O \xrightarrow[10\%\ H_2SO_4]{HgSO_4} CH_2 = CH - OH$$

$$CH_2 = CH - OH \rightsquigarrow CH_3 - \overset{\overset{O}{\|}}{C} - H$$

(ii) Acetone:

$$CH \equiv CH + NaNH_2 \longrightarrow CH \equiv \bar{C}\overset{+}{N}a + NH_3$$

$$CH \equiv \bar{C}\overset{+}{N}a + CH_3I \longrightarrow CH \equiv C - CH_3 + NaI$$

$$CH \equiv C - CH_3 + H_2O \longrightarrow CH_2 = \overset{\overset{OH}{|}}{C} - CH_3$$

$$CH_2 - \overset{\overset{OH}{|}}{C} - CH_3 \rightsquigarrow CH_3 - \overset{\overset{O}{\|}}{C} - CH_3$$

(iii) Ethyl Alcohol:

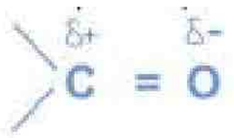
$$CH \equiv CH + H_2O \longrightarrow CH_2 = CH - OH$$

$$CH_2 = CH - OH \rightsquigarrow CH_3 - \overset{\overset{O}{\|}}{C} - H$$

$$CH_3 - \overset{\overset{O}{\|}}{C} - H + H_2 \xrightarrow{Pd} CH_3 - CH_2 - OH$$

35. Why carbonyl group is reactive?

Ans: The carbonyl group has a ϭ-bond and a π-bond. Thus it can undergo addition reactions. Most reagents react with the carbonyl group by adding to it. As oxygen is more electronegative, it tends to attract the π electrons to itself. This attraction makes the carbonyl group a polar group. The oxygen atom has a partial negative charge on it and is nucleophilic, whereas, the carbon atom has a partial positive charge and is electrophilic.



36. Give mechanism of nucleophilic addition reactions in aldehydes and ketones.

Ans:

37. Mention the tests for the identification of aldehydes.

Ans:

Tollen's Test [Silver Mirror Test]: Aldehydes form silver mirror with Tollen's reagent (ammoniacal silver nitrate solution). Add Tollen's reagent to an aldehyde solution in a test tube and warm. A silver mirror is formed on the inside of the test tube. High quality mirrors are manufactured by using this principle. Ketones do not give this test.

$$AgNO_3 + 3NH_4OH \rightarrow [Ag(NH_3)_2]OH + NH_4NO_3 + 2H_2O$$

$$R{-}CHO + 2[Ag(NH_3)_2]OH \rightarrow R\text{-}COONH_4 + 2Ag + 2NH_3 + H_2O$$

Silver mirror

Fehling's Solution Test [an alkaline solution containing a cupric tartrate complex ion]: Aliphatic aldehydes form a brick-red precipitate with Fehling's solution. To an aldehyde solution, add Fehling's solution and boil. A brick red precipitate of cuprous oxide is formed. Ketones do not give this test.

$$H - \overset{\overset{O}{\|}}{C} - H + 2Cu(OH)_2 + 2NaOH \longrightarrow HCOONa + Cu_2O + 3H_2O$$

(red ppt.)

Benedict's Solution Test |an alkaline solution containing a cupric

citrate complex ion]: Aliphatic aldehydes form a brick-red precipitate with Benedicts's solution. To an aldehyde solution, add Benedict's solution and boil. A brick-red precipitate of cuprous oxide is formed. Ketones do not give this test.

$$RCHO + 2Cu(OH)_2 + NaOH \rightarrow RCOONa + Cu_2O + 3H_2O$$

38. Mention the tests for the identification of ketones.

Ans:

Sodium Nitroprusside Test: Ketones produce a wine red or orange red colour on adding alkaline sodium nitroprusside solution dropwise. Aldehydes do not give this test.

39. Mention the tests for the identification of both aldehydes and ketones.

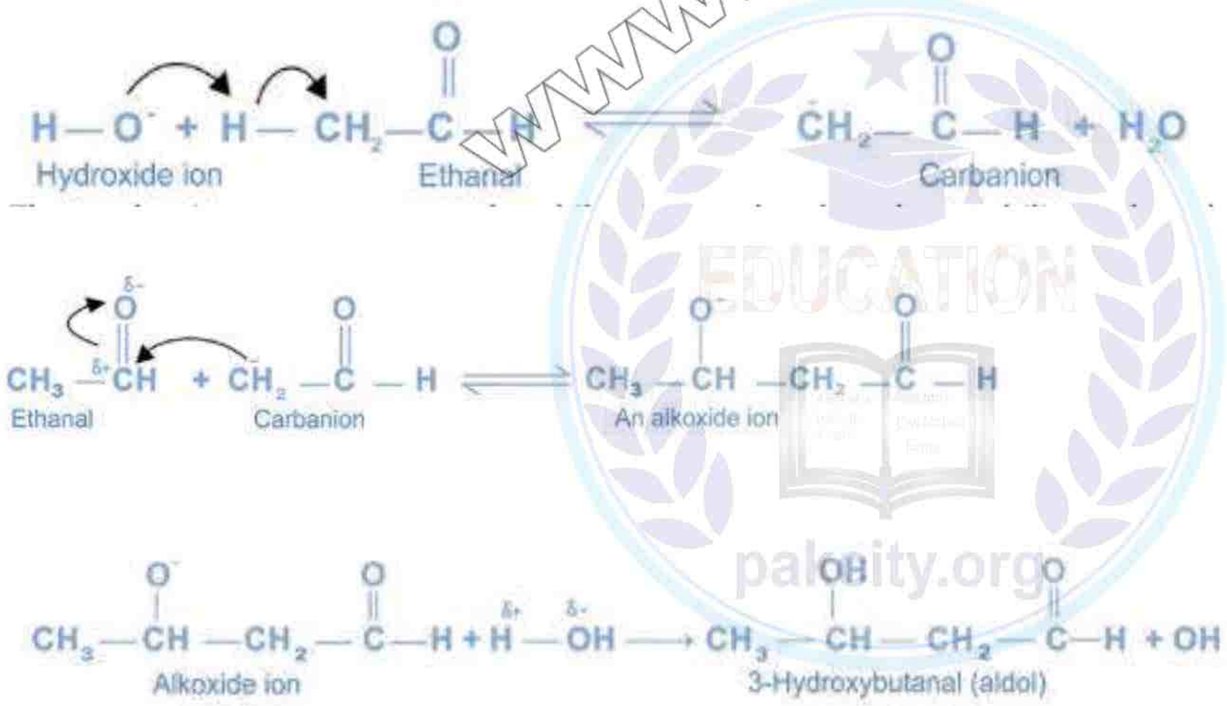
Ans:

1. 2,4 DNPH Test: Aldehydes and ketones form a yellow or red precipitate with 2,4 dinitrophenylhdrazine solution.

2. Sodium Bisulphite Test: Aldehydes and small methyl ketones form a crystalline white precipitate with saturated sodium bisulphite solution.

40. Give mechanism of aldol condensation.

Ans:



41. Give mechanism of Cannizzaro's reaction.

Ans: