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## Unit-10

## SURFACE CHEMISTRY

## 1. Give two important characteristics of physisorption

- (i) It is reversible.
- (ii) It takes place at low temperature and decreases with increase in temperature.
- (iii) It forms multimolecular layer.

## 2. Differentiate physisorption and chemisorption

physisorption	chemisorption
1. It is instantaneous 2. It is non-specific 3. Heat of adsorption is low in the order of 40kJ/mole. 4. Multilayer of the adsorbate is formed on the adsorbent. 5. It occurs on all sides.	1. It is very slow 2. It is very specific depends on nature of adsorbent and adsorbate. 3. Heat of adsorption is high i.e., from 40-400kJ/mole. 4. Monolayer of the adsorbate is formed. 5. Adsorption occurs at fixed sites called active centres. It depends on surface area

## 3. In case of chemisorption, why adsorption first increases and then decreases with temperature?

Chemisorption involves a high activation energy, so also referred to as activated adsorption. It is found in chemisorption that it first increases and then decreases.

4. Which will be adsorbed more readily on the surface of charcoal and why;  $\text{NH}_3$  or  $\text{CO}_2$ ?

Among  $\text{CO}_2$  and  $\text{NH}_3$ ,  $\text{NH}_3$  will be more readily adsorbed on the surface of the charcoal. This is because the critical temperature of ammonia gas is quite high than the carbon dioxide.

## 5. Heat of adsorption is greater for chemisorptions than physisorption. Why?

Chemisorption has higher enthalpy (from 40 - 400 kJ) of adsorption because in chemisorption the chemical bonds are much stronger. In adsorbed state the adsorbate is held on the surface of adsorbent by attractive forces (bond).

6. In a coagulation experiment 10 mL of a colloid (X) is mixed with distilled water and 0.1M solution of an electrolyte AB so that the total volume is 20 mL. It was found that all solutions containing more than 6.6 mL of AB coagulate within 5 minutes. What is the flocculation values of AB for sol (X)?

A minimum of 6.6 mL of AB is required to coagulate the sol.

$$\text{The moles of AB in the sol is} = \frac{6.6 \times 0.1}{20} = 0.033$$

This means that a minimum of 0.033 moles or  $0.033 \times 1000 = 33$  milli moles are required for coagulating 1 litre of sol. Therefore, Flocculation value of AB sol = 33.

## 7. Peptising agent is added to convert precipitate into colloidal solution. Explain with an example.

When peptising agent is added to freshly prepared precipitate, it changes into colloidal sol. It is called peptisation. During peptisation, the precipitate adsorbs one of the ions of the electrolyte on its surface.

**For example**, when we add a small volume of very dilute hydrochloric acid solution (peptizing agent) to a fresh precipitate of aluminum hydroxide.

**8. What happens when a colloidal sol of  $\text{Fe}(\text{OH})_3$  and  $\text{As}_2\text{O}_3$  are mixed?**

Mutual coagulation occurs which causes precipitation. This is because  $\text{Fe}(\text{OH})_3$  is positively charged and  $\text{As}_2\text{S}_3$  is negatively charged. When they are mixed, the particles get neutralised and get precipitated. No new compound is formed.

**9. What is the difference between a sol and a gel?**

In sol, dispersion medium is liquid and the dispersed phase is solid. In gel, dispersion medium is solid and dispersed phase is liquid.

**10. Why are lyophilic colloidal sols more stable than lyophobic colloidal sol.**

In lyophobic colloids, no attractive force exists between the dispersed phase and dispersion medium. They are less stable and precipitated readily, but not be produced again by just adding the dispersion medium. They themselves undergo coagulation after a span of characteristic life time. They are called irreversible sols.

examples: sols of gold, silver, platinum and copper

**11. Addition of Alum purifies water. Why?**

Purification of drinking water is activated by coagulation of suspended impurities in water using alums containing  $\text{Al}^{3+}$ .

**12. What are the factors which influence the adsorption of a gas on a solid?**

The adsorption is well understood by considering the various factors affecting it. Qualitatively, the extent of surface adsorption depends on

- (i) Nature of adsorbent
- (ii) Nature of adsorbate
- (iii) Pressure
- (iv) Concentration at a given temperature.

**13. What are enzymes? Write a brief note on the mechanism of enzyme catalysis.**

Enzymes are complex protein molecules with three dimensional structures. They catalyse the chemical reaction in living organism. They are often present in colloidal state and extremely specific in catalytic action.

**Mechanism of enzyme catalysed reaction**

The following mechanism is proposed for the enzyme catalysis



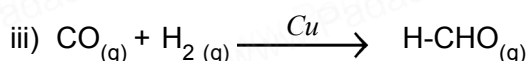
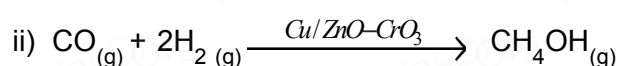
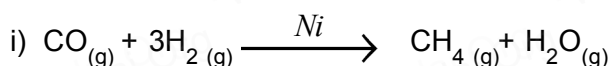
Where E is the enzyme, S the substrate (reactant), ES represents activated complex and P the products.

**14. What do you mean by activity and selectivity of catalyst?****(a) Activity of a catalyst:**

The activity of a catalyst is its ability to increase the rate of a particular reaction. Chemisorption is the main factor in deciding the activity of a catalyst. The adsorption of reactants on the catalyst surface should be neither too strong nor too weak. It should just be strong enough to make the catalyst active.

**(b) Selectivity of the catalyst:**

The ability of the catalyst to direct a reaction to yield a particular product is referred to as the selectivity of the catalyst. **For example**, by using different catalysts, we can get different products for the reaction between  $\text{H}_2$  and CO.



**15. Describe some feature of catalysis by Zeolites.**

Zeolites are hydrated aluminosilicates, made of silicon and aluminium tetrahedra.

- i) There are about 50 natural zeolites and 150 synthetic zeolites.
- ii) As silicon is tetravalent and aluminium is trivalent, the zeolite matrix carries extra negative charge.
- iii) To balance the negative charge, there are extra framework cations for example,  $H^+$  or  $Na^+$  ions.
- iv) Zeolites carrying protons are used as solid acids, catalysis and they are extensively used in the
- v) petrochemical industry for cracking heavy hydrocarbon fractions into gasoline, diesel, etc.,
- vi) Zeolites carrying  $Na^+$  ions are used as basic catalysis.
- vii) One of the most important applications of zeolites is their shape selectivity. In zeolites, the active sites namely protons are lying inside their pores. So, reactions occur only inside the pores of zeolites.

**16. Give three uses of emulsions.**

- (i) Cleansing action of soaps is based on the formation of emulsions.
- (ii) Digestion of fats in intestines takes place by the process of emulsification.
- (iii) Antiseptics and disinfectants when added to water form emulsions.
- (iv) The process of emulsification is used to make medicines.

**17. Why does bleeding stop by rubbing moist alum**

Blood is a colloidal sol. When we rub the injured part with moist alum then coagulation of blood takes place. Hence, main reason is coagulation, which stops the bleeding

**18. Why is desorption important for a substance to act as good catalyst?**

Desorption is important for a substance to act as a good catalyst so that after the reaction, the products formed on the surface separate out (desorbed) to create free surface again for other reactant molecules.

If desorption does not occur then other reactants are left with no space on the catalyst's surface for adsorption and reaction will stop.

**19. Comment on the statement: Colloid is not a substance but it is a state of substance.**

Common salt (a typical crystalloid in an aqueous medium) behaves as a colloid in a benzene medium. Hence, we can say that a colloidal substance does not represent a separate class of substances. When the size of the solute particle lies between 1 nm and 1000 nm, it behaves as a colloid.

Hence, we can say that colloid is not a substance but a state of the substance which is dependent on the size of the particle. A colloidal state is intermediate between a true solution and a suspension.

**20. Explain any one method for coagulation**

Clotting is what prevents excessive bleeding when you cut yourself. But the blood moving through your vessels shouldn't clot. If such clots form, they can travel through your bloodstream to your heart, lungs, or brain. This can cause a heart attack, stroke, or even death.

Coagulation tests measure your blood's ability to clot, and how long it takes to clot. Testing can help your doctor assess your risk of excessive bleeding or developing clots (thrombosis) somewhere in your blood vessels.

**21. Write a note on electro osmosis**

Electro-osmosis is the migration of water (and whatever is contained in the water) through a porous membrane resulting from a potential difference caused by the flow of electric charge through the membrane.

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**22. Write a note on catalytic poison**

Certain substances when added to a catalysed reaction decrease or completely destroy the activity of catalyst and they are often known as catalytic poisons.

**23. Explain intermediate compound formation theory of catalysis with an example****The intermediate compound formation theory**

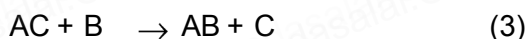
A catalyst acts by providing a new path with low energy of activation. In homogeneous catalysed reactions a catalyst may combine with one or more reactant to form an intermediate

which reacts with other reactant or decompose to give products and the catalyst is regenerated.

Consider the reactions:



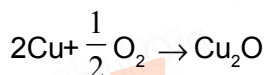
C is the catalyst



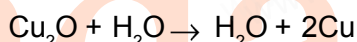
Activation energies for the reactions (2) and (3) are lowered compared to that of (1). Hence the formation and decomposition of the intermediate accelerate the rate of the reaction.

**Example**

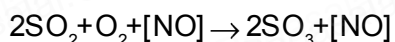
Formation of water due to the reaction of  $H_2$  and  $O_2$  in the presence of Cu can be given as



It is an intermediate.

**24. What is the difference between homogenous and heterogeneous catalysis?****Homogeneous catalysis**

In a catalysed reaction, the reactants, products and catalyst are present in the same phase.

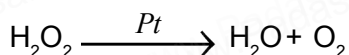
**Illustration**

In this reaction the catalyst NO, reactants,  $SO_2$  and  $O_2$ , and product,  $SO_3$  are present in the gaseous form.

**Heterogeneous catalysis**

In a reaction, the catalyst is present in a different phase i.e. It is not present in the same phase as that of reactants or products.

Decomposition of  $H_2O_2$  occurs in the presence of the Pt catalyst

**25. Describe adsorption theory of catalysis.****Adsorption theory**

Langmuir explained the action of catalyst in heterogeneous catalysed reactions based on adsorption. The reactant molecules are adsorbed on the catalyst surfaces, so this can also be called as contact catalysis.

According to this theory, the reactants are adsorbed on the catalyst surface to form an activated complex which subsequently decomposes and gives the product.

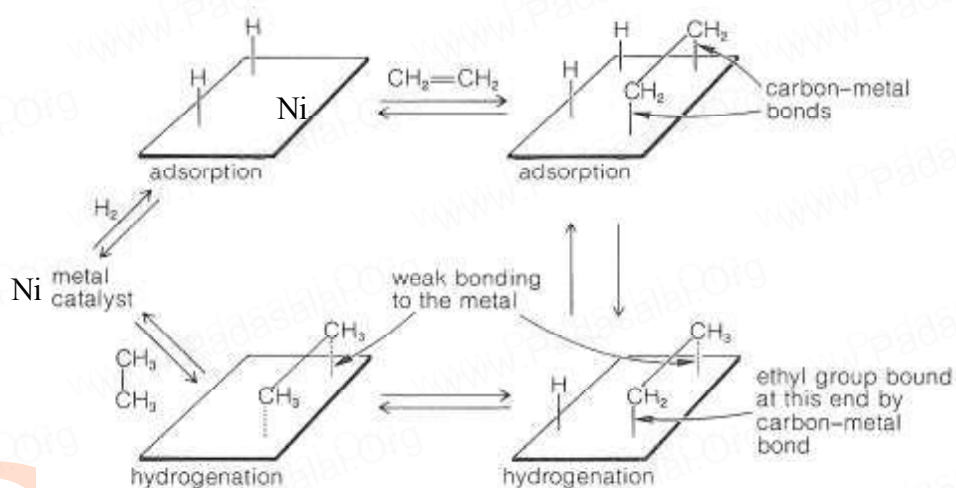
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**The various steps involved in a heterogeneous catalysed reaction are given as follows:**

1. Reactant molecules diffuse from bulk to the catalyst surface.
2. The reactant molecules are adsorbed on the surface of the catalyst.
3. The adsorbed reactant molecules are activated and form activated complex which is decomposed to form the products.
4. The product molecules are desorbed.
5. The product diffuse away from the surface of the catalyst.

**eg ) Hydrogenation of ethylene in presence of a nickel catalyst.**



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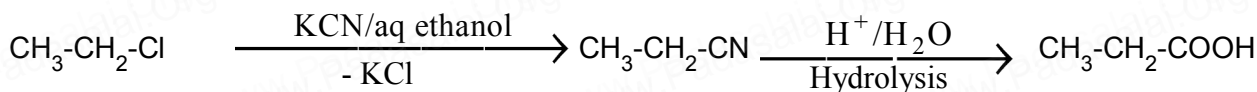
**CARBONYL COMPOUNDS AND CARBOXYLIC ACIDS**

1. How is propanoic acid is prepared starting from  
 (a) an alcohol (b) an alkylhalide (c) an alkene

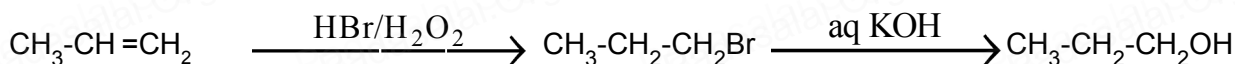
**a) An Alcohol converted in to propanoic acid**



**b) An alkyl halide converted in to propanoic acid**

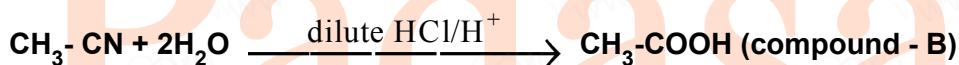


**c) An alkene converted in to propanoic acid**

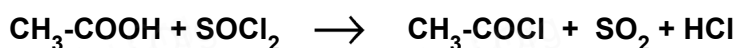


2. A Compound (A) with molecular formula  $\text{C}_2\text{H}_3\text{N}$  on acid hydrolysis gives (B) which reacts with thionylchloride to give compound (C). Benzene reacts with compound (C) in presence of anhydrous  $\text{AlCl}_3$  to give compound (D). Compound (D) on reduction with gives (E). Identify (A), (B), (C) and D, E Write the equations.

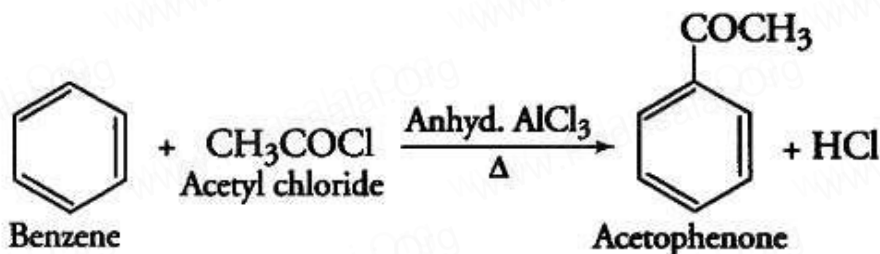
**Compound (A) is nitrile (  $\text{CH}_3\text{CN}$  )**



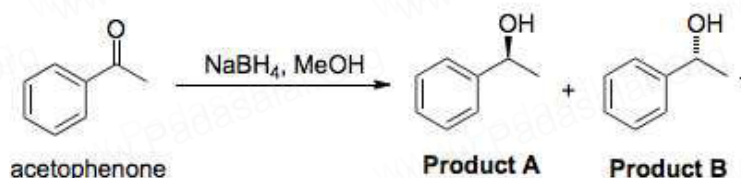
**Compound (B) gives Compound (C)**



**Compound (C) gives Compound (D)**



**Compound (D) gives Compound (E)**



**Compound (A)- Nitrile**

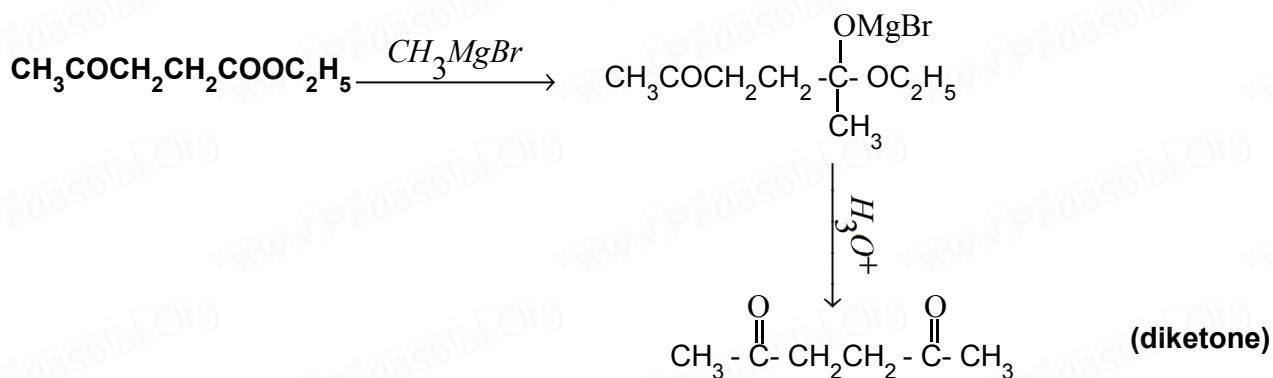
**Compound (C)- Acetyl chloride**

**Compound (E) - Methyl phenyl carbinol**

**Compound (B) - Acetic acid**

**Compound (D) - Acetophenone**

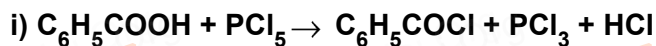
3. Identify X and Y.  $\xrightarrow{CH_3MgBr} X \xrightarrow{H_3O^+}$



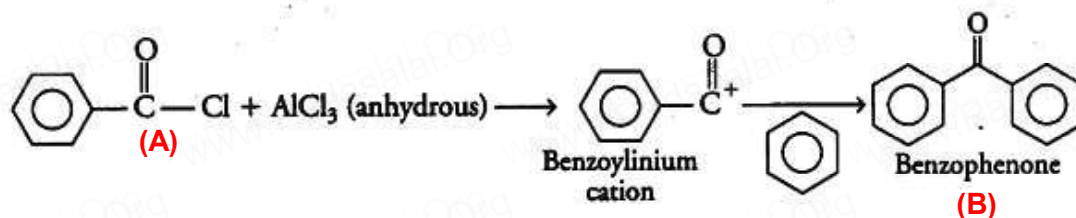
4. Identify A, B and C, Benzoic acid  $\xrightarrow{PCl_5}$  A  $\xrightarrow[\text{anhydrous } AlCl_3]{\text{benzene}}$  B

$\downarrow C_2H_5OH/H^+$   
 C  $\xrightarrow{C_6H_5MgBr}$  B

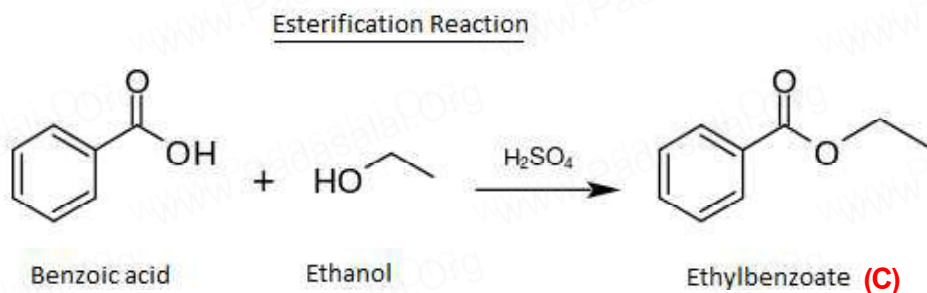
i) benzoic acid to A



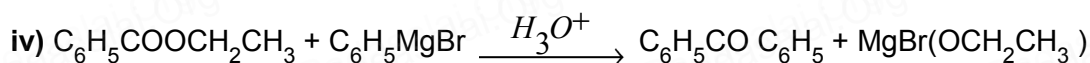
ii)  $C_6H_5COCl$  (A) to Benzophenone (B)



iii) benzoic acid to C



(C) to Benzophenone



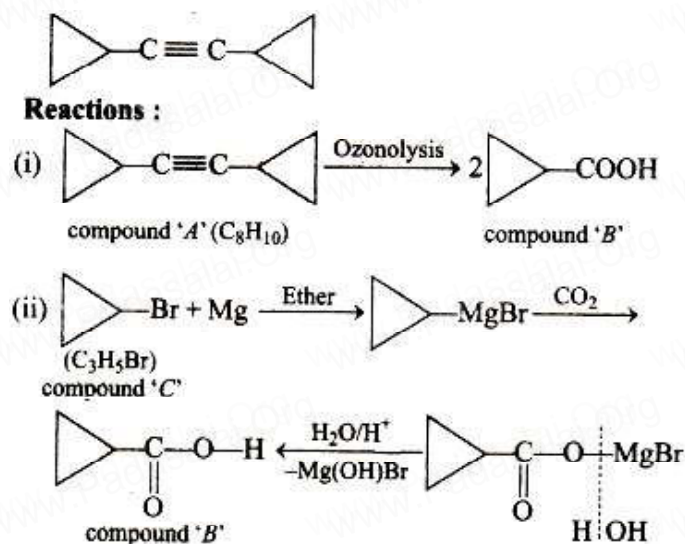
A -  $C_6H_5COCl$  ( Benzoyl chloride )

B- Benzophenone

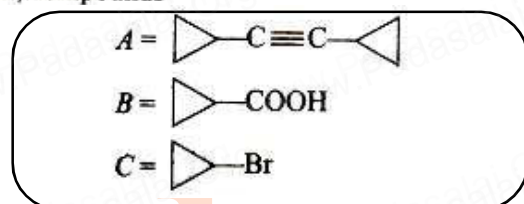
C - Ethyl benzoate



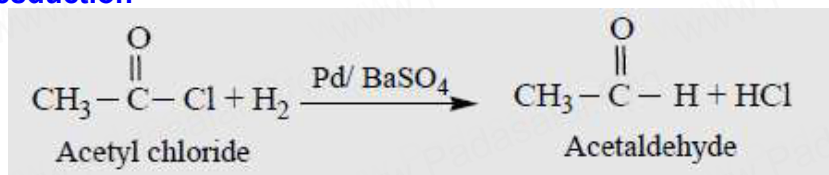
5. A hydrocarbon A (molecular formula  $C_8H_{10}$ ) on ozonolysis gives B ( $C_4H_6O_2$ ) only. Compound C ( $C_3H_5Br$ ) on treatment with magnesium in dry ether gives (D) which on treatment with  $CO_2$  followed by acidification gives (C). Identify A, B and C.



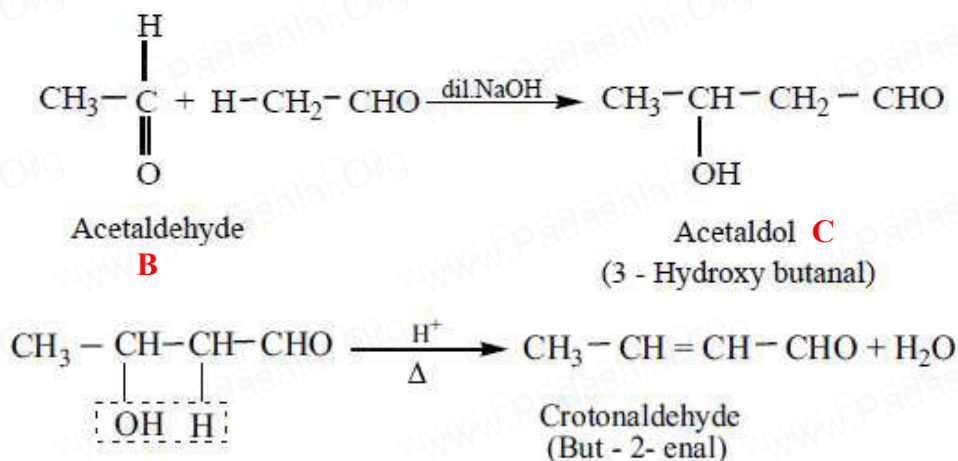
Thus, compounds



6. Identify A, B, C and D
- ethanoic acid  $\xrightarrow{SOCl_2}$  A  $\xrightarrow{Pd/BaSO_4}$  B  $\xrightarrow{NaOH}$  C  $\xrightarrow{\Delta}$  D
- i)  $CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$
- ii) **Rosenmund reduction**



iii) **Aldol condensation**



A- Acetyl Chloride

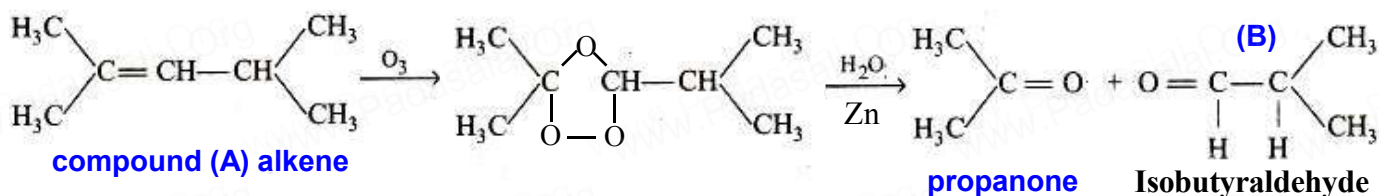
B- Acetaldehyde

C- Aldol

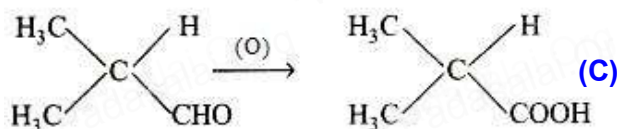
D - Crotonaldehyde

7. An alkene (A) on ozonolysis gives propanone and aldehyde (B). When (B) is oxidised (C) is obtained. (C) is treated with  $\text{Br}_2/\text{red-P}$  gives (D) which on hydrolysis gives (E). When propanone is treated with HCN followed by hydrolysis gives (E). Identify A, B, C, D and E.

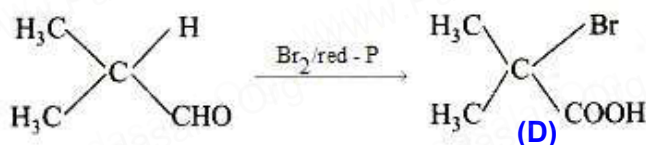
i) An alkene (A) on ozonolysis gives propanone and aldehyde (B) is



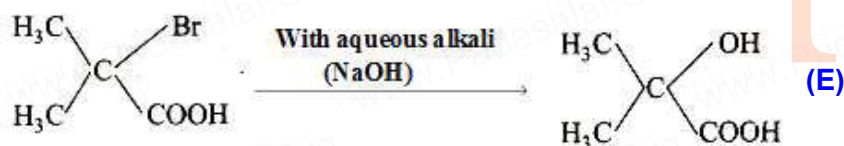
ii) (B) is oxidised to give (C) is Isobutyric acid



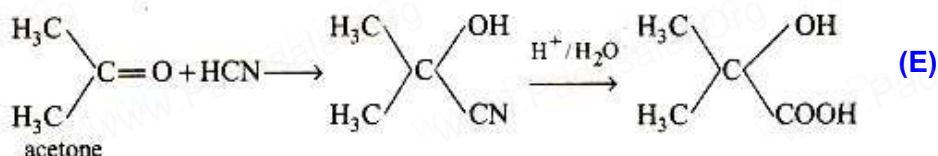
iii) Hell – Volhard – Zelinsky reaction (HVZ reaction) The  $\alpha$ - Halogenated acids are convenient starting materials for preparing  $\alpha$  - substituted acids.



iv) (D) which on hydrolysis gives (E). (hydrolysis of 'D' with aqueous alkali)



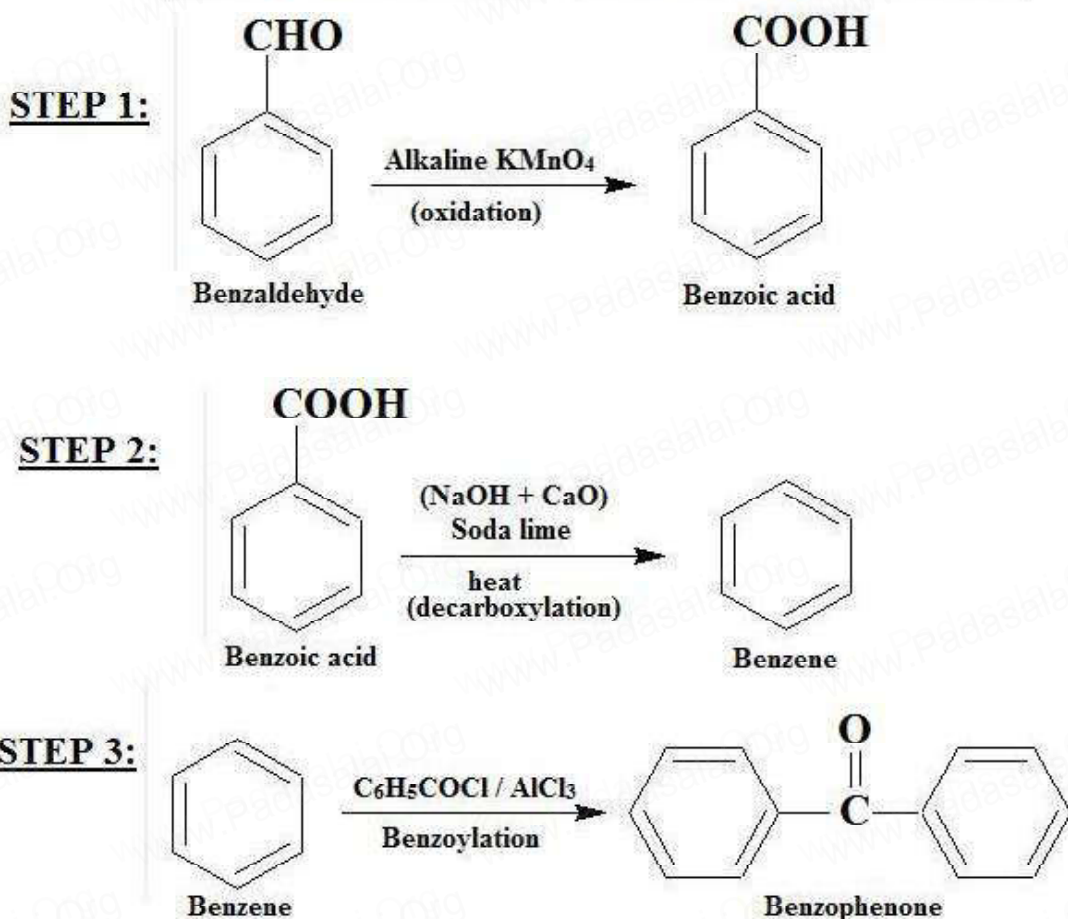
v) propanone is treated with HCN followed by hydrolysis gives (E)



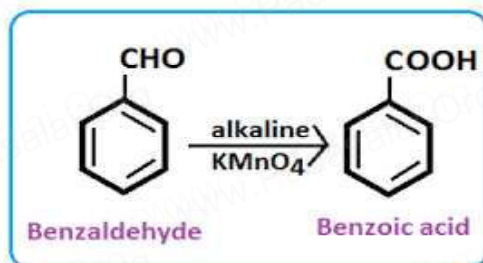
Compound - A	- unsymmetrical alkene
Compound - B	- Isobutyraldehyde
Compound - C	- Isobutyric acid
Compound - D	- 2-Bromo-2-methyl propionic acid
Compound - E	- 2-methyl -2- hydroxy propanoic acid

8. How will you convert benzaldehyde into the following compounds?  
 (i) benzophenone (ii) benzoic acid (iii)  $\alpha$ -hydroxyphenylacetic acid.

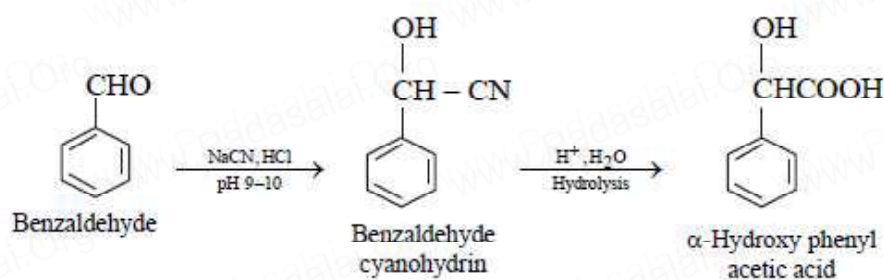
### Conversion of benzaldehyde to benzophenone



i) Benzaldehyde into Benzoic acid



i) Benzaldehyde into Benzoic acid



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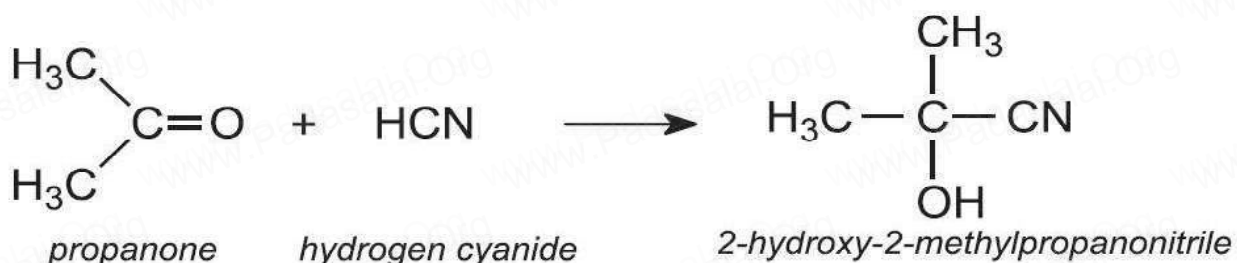
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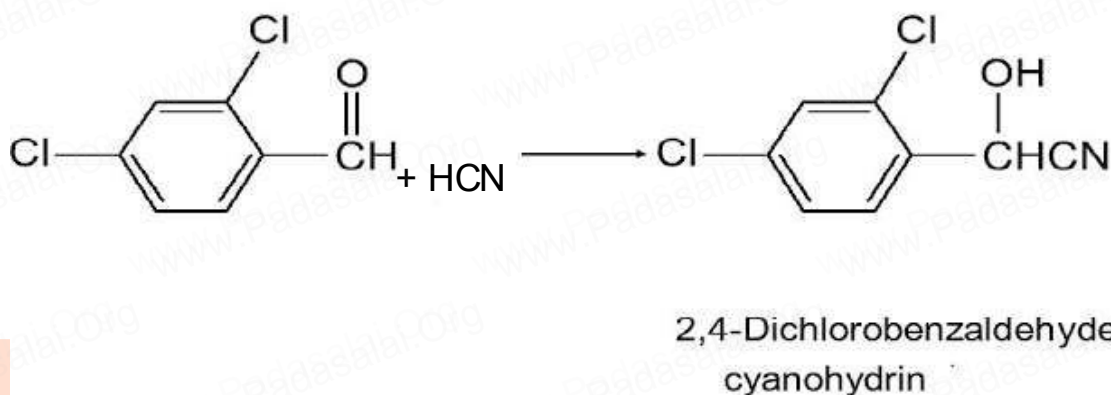
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9. What is the action of HCN on  
 (i) propanone (ii) 2,4-dichlorobenzaldehyde. (iii) ethanal

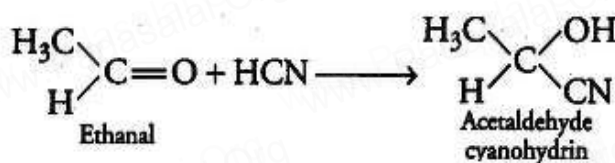
**i) Action of HCN on propanone**



**ii) Action of HCN on 2,4-dichlorobenzaldehyde.**



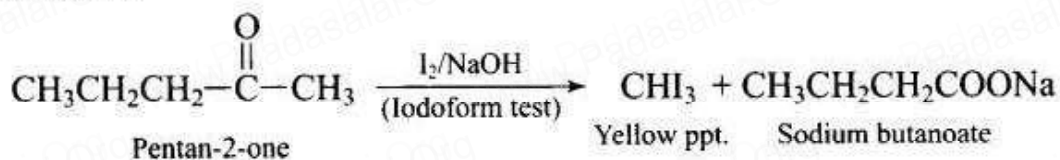
**iii) Action of HCN on ethanal**



10. A carbonyl compound A having molecular formula  $\text{C}_5\text{H}_{10}\text{O}$  forms crystalline precipitate with sodium bisulphate and gives positive iodoform test. A does not reduce Fehling solution. Identify A.

It does not reduce fehling's solution but forms bisulphite compound so it is a ketone therefore it gives positive iodoform test therefore it is methyl ketone.

Pentan-2-one having a  $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—CH}_3$  group forms a yellow ppt. of iodoform with an alkaline solution of iodine (i.e., iodoform test) while pentan-3-one does not.



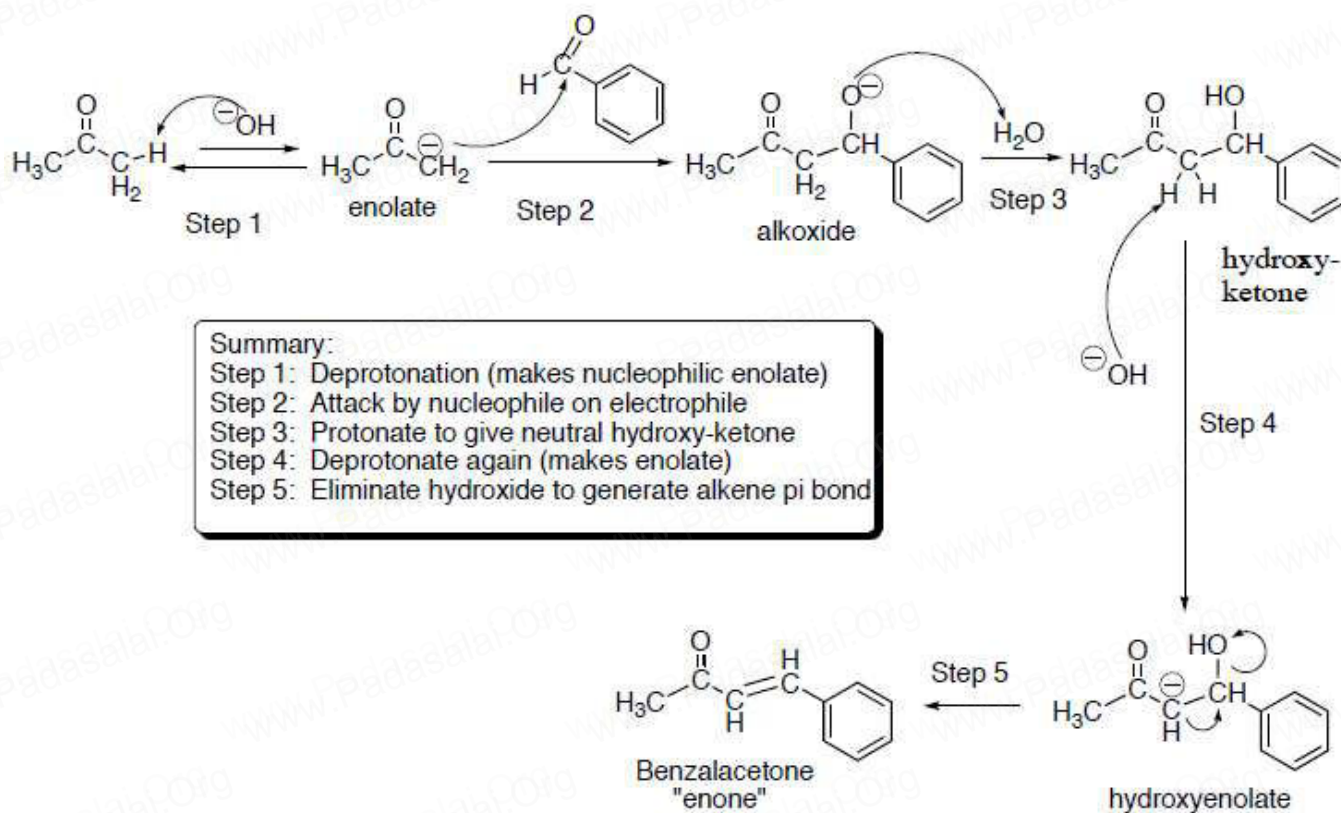
**Ans: Compound A is Pentan-2-one**

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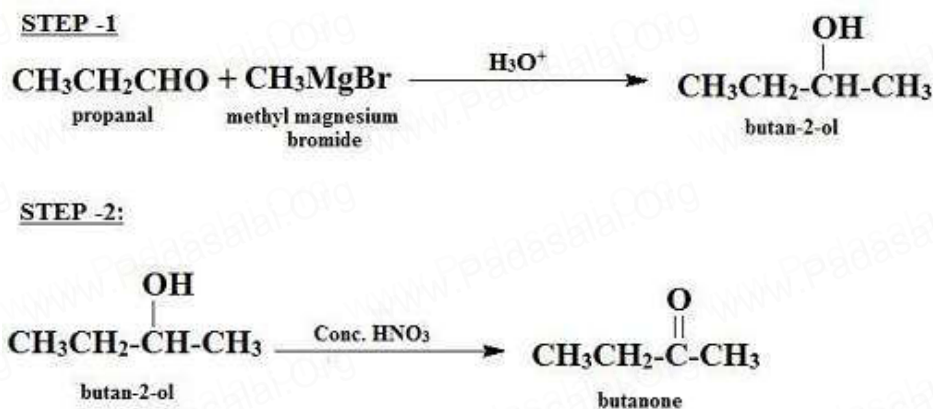


11. Write the structure of the major product of the aldol condensation of benzaldehyde with acetone.

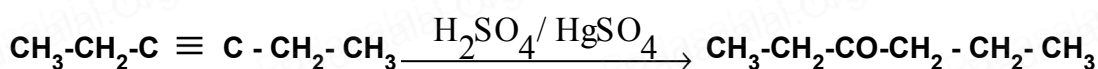


12. How are the following conversions effected
- propanal into butanone
  - Hex-3-yne into hexan-3-one.
  - phenylmethanal into benzoic acid
  - phenylmethanal into benzoin
- (a) propanal into butanone

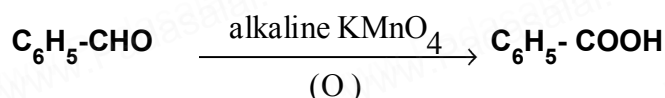
Conversion of propanal to butanone



- (b) Hex-3-yne into hexan-3-one.



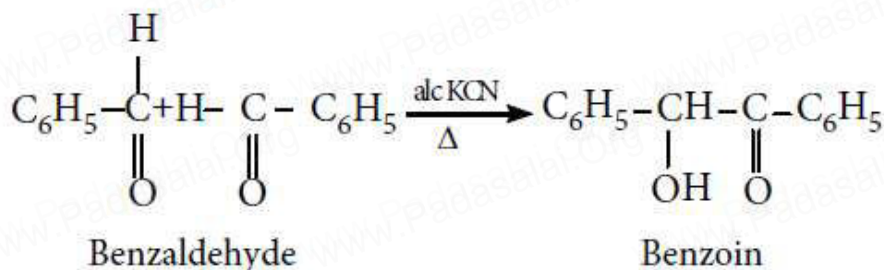
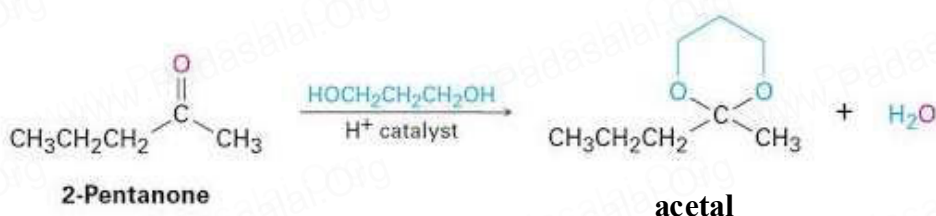
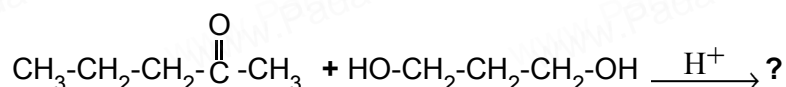
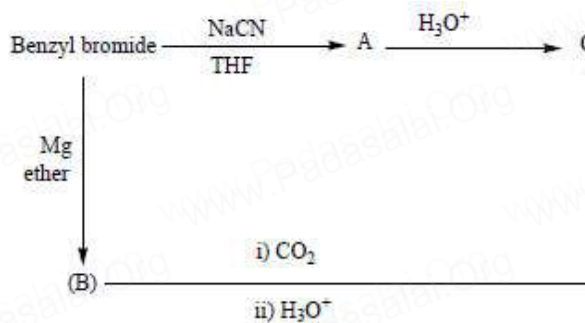
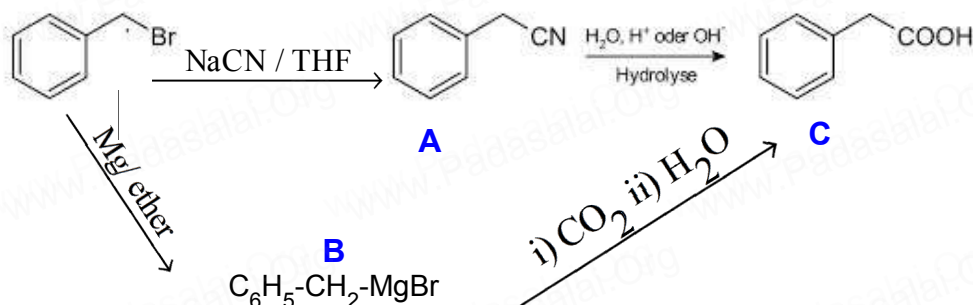
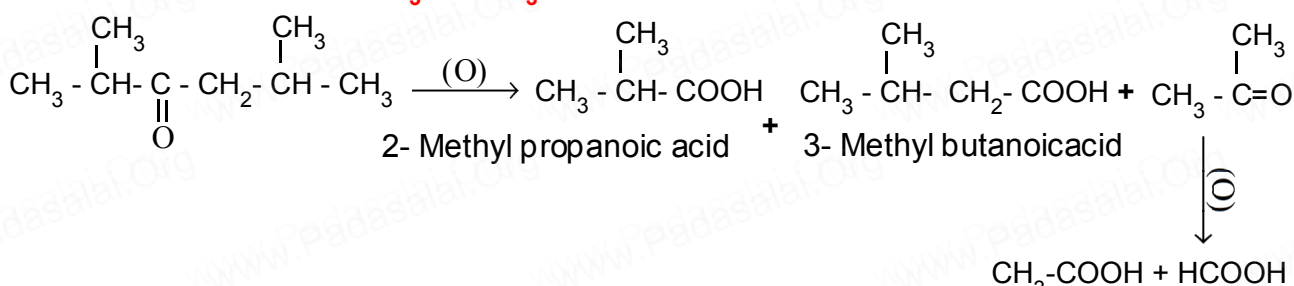
- (c) phenylmethanal into benzoic acid





**Phenylmethanal into benzoin**

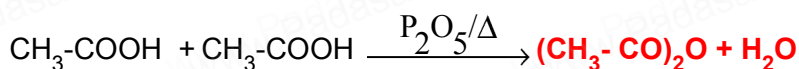
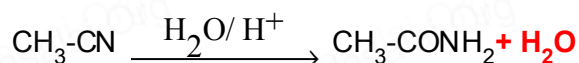
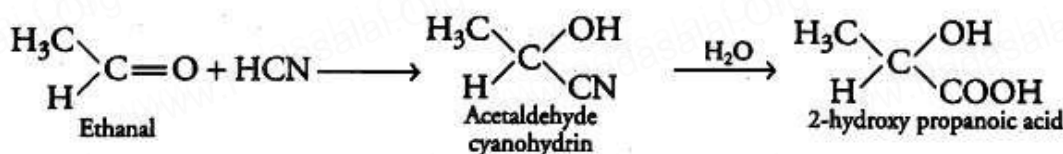
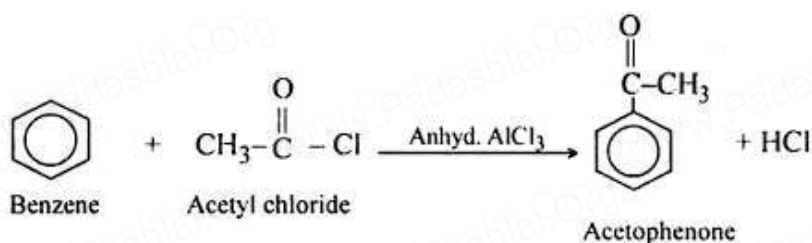
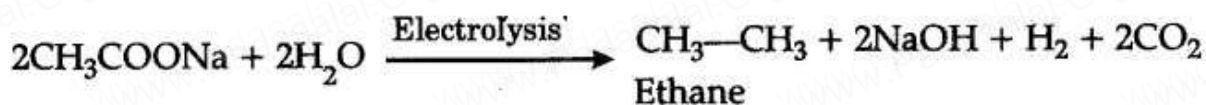
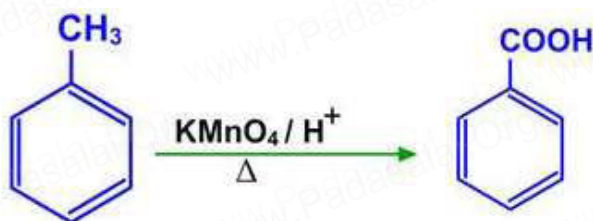
Benzaldehyde reacts with alcoholic KCN to form benzoin

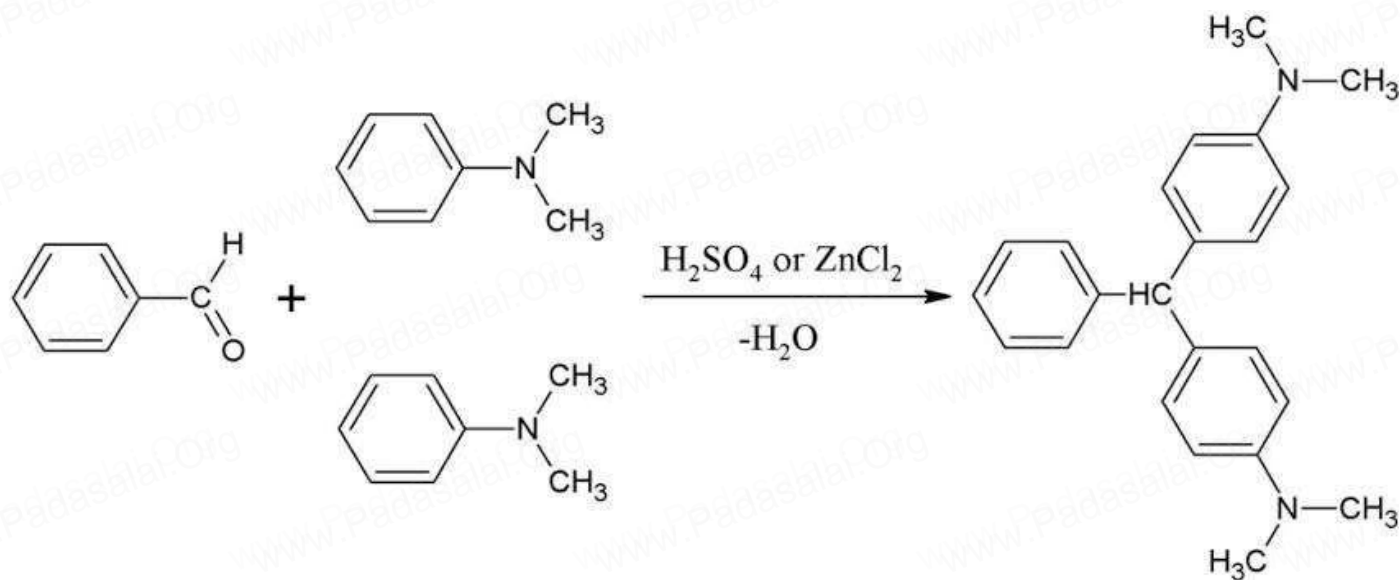
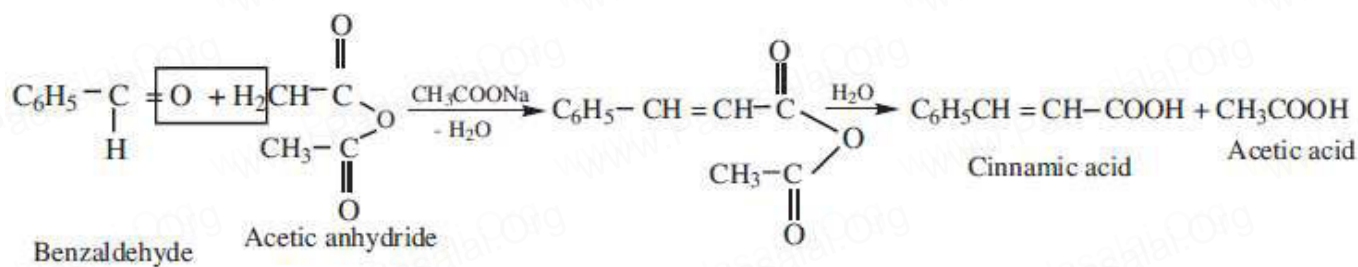
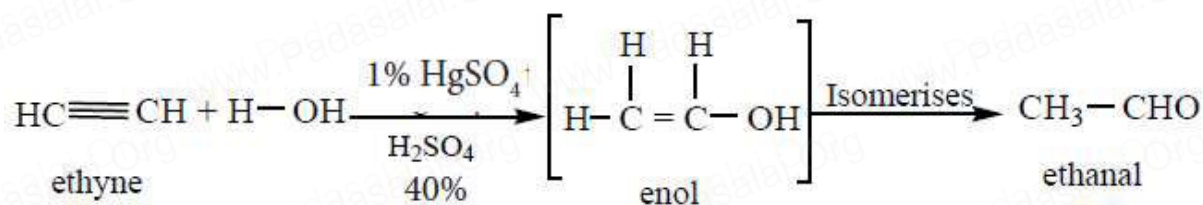
**13. Complete the following reaction.****14. Identify A, B and C****Soln:****A - Benzyl cyanide    B - Benzyl magnesium bromide    C) 2 - Phenyl ethanoic acid****15. Oxidation of ketones involves carbon – carbon bond cleavage. Name the product (s) is / are formed on oxidising 2,5 – dimethylhexan – 2 – one using strong oxidising agent .****According to Popoff's rule, the unsymmetrical ketone on oxidation, C-C bond cleavage and keto group goes with CH<sub>3</sub>-CH(CH<sub>3</sub>)-**

## 16. How will you prepare

- i. Acetic anhydride from acetic acid
- iii. Acetamide from methylcyanide
- v. Acetophenone from acetylchloride
- vii. Benzoic acid from toluene
- ix. Cinnamic acid from benzaldehyde

- ii. Ethylacetate from methylacetate
- iv. Lactic acid from ethanal
- vi. Ethane from sodium acetate
- viii. Malachitegreen from benzaldehyde
- x. Acetaldehyde from ethyne

**i. Acetic anhydride from acetic acid****ii. Ethylacetate from methylacetate****iii. Acetamide from methylcyanide****iv. Lactic acid from ethanal****v. Acetophenone from acetylchloride****vi. Ethane from sodium acetate****vii. Benzoic acid from toluene**

**viii. Malachitegreen from benzaldehyde****ix. Cinnamic acid from benzaldehyde****x. Acetaldehyde from ethyne****S.SHANMUGAM , PG Assistant****Dept of Chemistry****St.John's M.H.S.S porur Chennai -116****Mob: 9841945665**