

**CHEMISTRY**

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**ADVANTAGE KOTA**

11 - 12 SCI

IIT - JEE

GUJCET

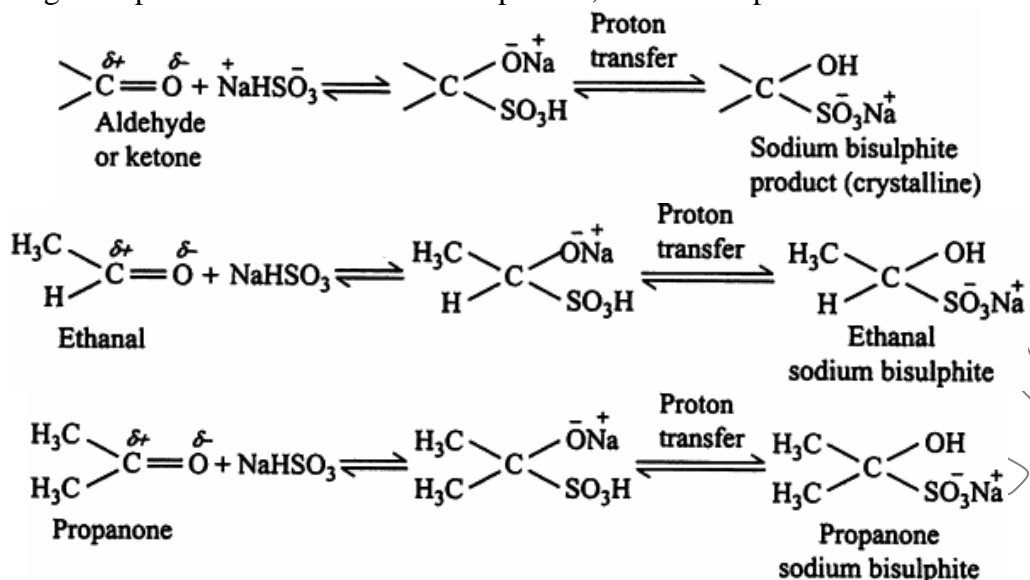
GSEB

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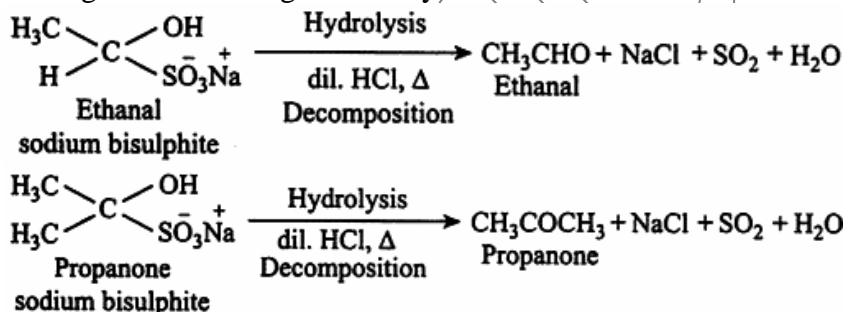
Eng - Med / Guj - Med

(1) **Explain: Addition of sodium hydrogen sulphite (NaHSO<sub>3</sub>)**

**Sol:** Due to less steric hindrance most of the aldehydes and aliphatic methyl ketones, react with sodium hydrogen sulphite and form additive compounds, while acetophenone does not react.



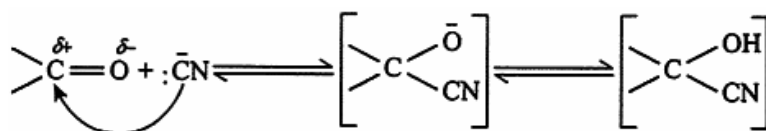
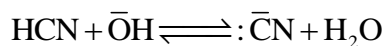
➤ If bisulphite product is heated with dilute mineral acid or aqueous alkaline they decompose, due to hydrolysis and regenerate the original aldehyde or ketone.



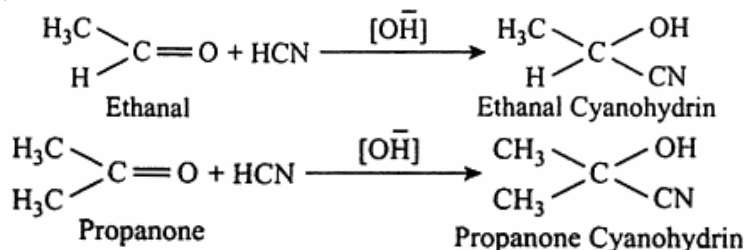
➤ Therefore, this reaction is useful for the separation and purification of aldehydes and ketones from non-carbonyl compounds.

(2) **Explain: Addition of Hydrogen Cyanide (HCN)**

**Sol:** Aldehydes and ketones react with hydrogen cyanide and give product cyanohydrin. The reaction is extremely slow and so it is carried out in presence of base which acts as a catalyst. The reaction occurs very slowly with pure HCN but in presence of base (as a catalyst) the CN<sup>-</sup> is generated which is a stronger nucleophile and gets added readily to carbonyl compounds and the product cyanohydrin is obtained. For example,

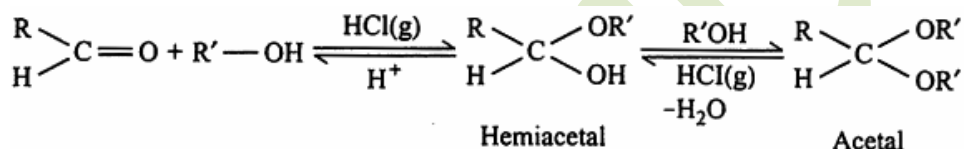


➤ Cyanohydrins are important synthetic substances because they can be readily hydrolyzed to give 2-hydroxy acids.

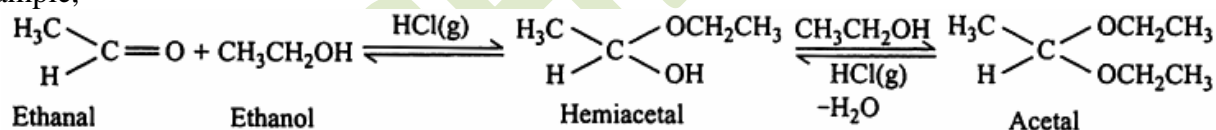


### (3) Explain: Addition of alcohol

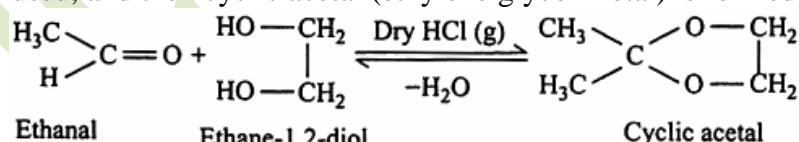
**Sol:** Aldehyde reacts with one equivalent of monohydric alcohol in presence of dry hydrogen chloride to yield alkoxy alcohol intermediate known as hemiacetal (hemi means half). Being unstable it immediately reacts with one more molecule of alcohol to form stable gem-di alkoxy compound known as acetal.



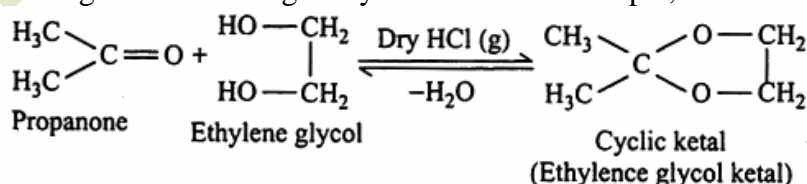
➤ Dry hydrogen chloride protonates the oxygen of aldehyde (carbonyl compound) hence the density of positive charge on carbonyl carbon increases i.e. the electro positivity of carbonyl carbon increases, which facilitates the nucleophilic attachment. Dry HCl gas absorbs the water molecules which is produced during acetal formation and shifts the equilibrium in the forward direction. For example,



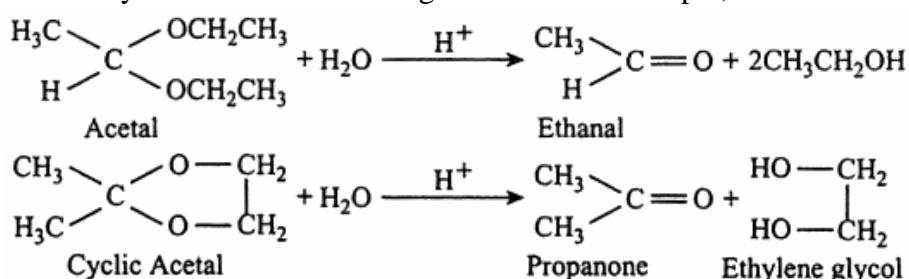
➤ Instead of two molecules of monohydric alcohol in presence of dry hydrochloric acid or paratoluene sulphonic acid (PTS), one molecule of dihydric alcohol such as ethane-1, 2-diol (ethylene glycol) is used, and then cyclic acetal (ethylene glycol-ketal) is formed.



➤ Ketones do not react with monohydric alcohols but react with dihydric alcohols in presence of dry hydrochloric acid gas or PTS and give cyclic ketal. For example,

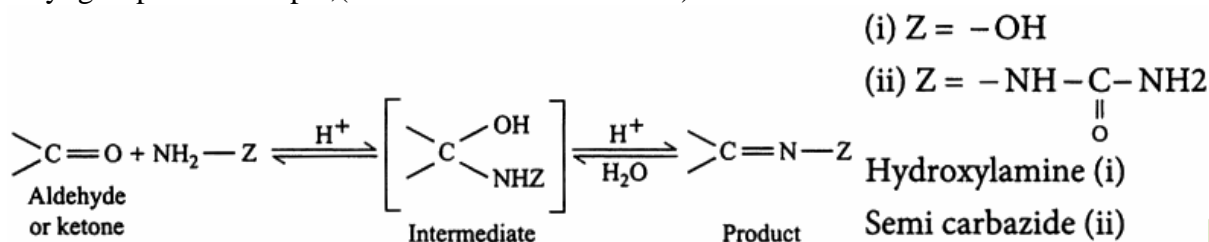


➤ In the formation of acetal and ketal the reactions are reversible; so they are decomposed by dilute acid and the aldehydes and ketones are regenerated. For example,



(4) **Explain: Addition of ammonia and its derivatives**

**Sol:** Aldehydes and ketones react with ammonia and its derivatives. The reaction is catalyzed by acid, hence the carbonyl groups gets protonated, so the positive charge on carbonyl carbon is increased and as a result the weak nucleophile like ammonia and its derivatives readily attach to the carbonyl group. For example, (draw table form text book)



(5) **Explain reactivity of aldehydes and ketones.**

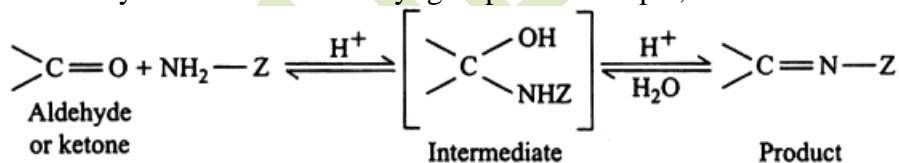
**Sol:** Aldehydes and ketones have the same functional group i.e. polarized carbonyl group. So they undergo similar chemical reactions. However, the presence of hydrogen atom on the carbonyl group of aldehydes makes them much more reactive than ketones. This hydrogen atom is responsible for many reactions of aldehydes and thus they differ from ketones.

(6) **Explain nucleophilic addition reactions followed by elimination of a molecule of water for aldehydes and ketones.**

**Sol:** Aldehydes and ketones have the carbonyl group containing double bond and so they can undergo addition reaction.

➤ Aldehydes and ketones undergo nucleophilic addition reactions because the carbonyl group is polar and carbon atom is slightly positively charged which is readily attracted by the nucleophile.

➤ Addition of ammonia and its derivatives: Aldehydes and ketones react with ammonia and its derivatives. The reaction is catalyzed by acid, hence the carbonyl groups gets protonated, so the positive charge on carbonyl carbon is increased and as a result the weak nucleophile like ammonia and its derivatives readily attach to the carbonyl group. For example,



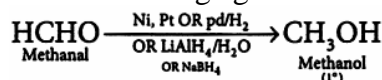
The equilibrium favours the product formation due to rapid dehydration of the intermediate to form (=C=N-Z).

(7) **Explain reductions of aldehydes.**

**Sol:** Aldehydes on reduction forms either primary alcohol or hydrocarbon depending on the reaction condition.

(i) **Reduction to alcohol**

➤ Aldehyde on reduction gives 1° alcohols. Reduction is carried out either catalytically with H<sub>2</sub> in presence of Ni, Pt or Pd or chemically lithium aluminium hydride (LiAlH<sub>4</sub>) or sodium borohydride (NaBH<sub>4</sub>). LiAlH<sub>4</sub> is a much more powerful reducing agent than NaBH<sub>4</sub>.

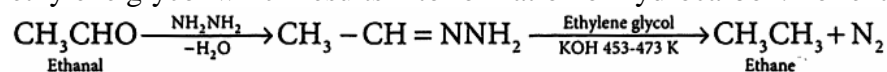


(ii) **Reduction to hydrocarbon:**

➤ The carbonyl group of aldehydes is reduced to methylene (-CH<sub>2</sub>-) group to form hydrocarbon by using different reducing agent.

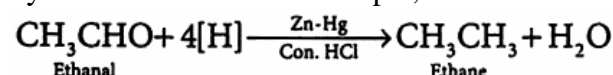
(a) **Wolff-Kishner reduction:**

➤ Aldehyde or ketone is heated with hydrazine (NH<sub>2</sub>NH<sub>2</sub>) and KOH in high boiling solvent like ethylene glycol which results into formation of hydrocarbon. For example,



(b) **Clemmensen reduction:**

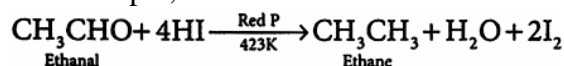
➤ Aldehyde is reduced to hydrocarbon, on treatment with zinc amalgam and concentrated hydrochloric acid. For example,



(c) **Reduction with HI and Red P:**

➤ Aldehyde when heated with hydroiodic acid and red phosphorous is reduced to hydrocarbon.

For example,

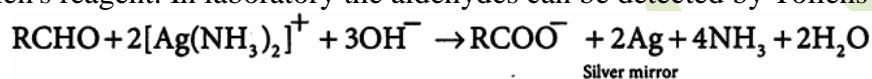


(2) **Explain oxidation of aldehydes.**

**Sol:** Aldehydes are easily oxidized to carboxylic acids containing the same number of carbon atoms, because of the presence of hydrogen atom on carbonyl group which is converted to -OH group, without involving the cleavage of any other bond. So they easily get oxidized by both strong and weak oxidizing agent. Oxidation of aldehydes:

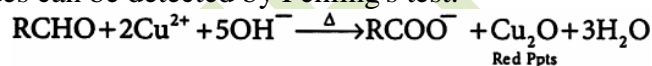
(i) **Tollens' test:**

➤ Aldehyde and freshly prepared ammoniacal silver nitrate solution (Tollen's reagent) when gently warmed, the aldehyde is oxidized to carboxylate ion, and Tollens' reagent is reduced to metallic silver which gets deposited on the inner wall of test-tube giving shining surface like mirror. Hence this test is also known as silver mirror test. Aromatic and aliphatic aldehydes are both oxidized by Tollens' reagent. In laboratory the aldehydes can be detected by Tollens' test.



(ii) **Fehling's test:**

➤ Fehling solution A ( $\text{CuSO}_4$  solution) and Fehling solution B (alkaline solution of sodium potassium tartarate-Rochelle salt) are mixed in equal proportion and the mixture is heated with aldehyde, giving red precipitates of cuprous oxide. This test is known as Fehling's test. This test is only for aliphatic aldehydes because the aromatic aldehydes are not reduced by the Fehling solution. In laboratory the aldehydes can be detected by Fehling's test.



(iii) **Benedict's test:**

➤ This test is similar to Fehling's test but instead of tartarate ions the citrate ions were used. The reduction is same and this test is also not given by aromatic aldehydes.

(8) **Explain oxidation of ketones.**

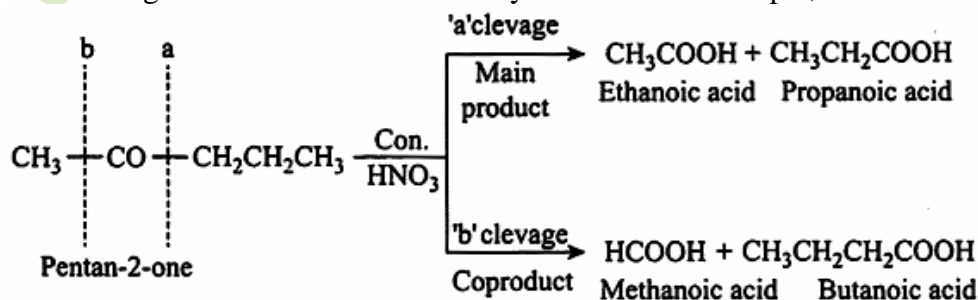
**Sol:** Ketones can be oxidized by powerful oxidizing agent only, because during oxidation carbon-carbon bond cleavage results into mixture of carboxylic acids, each containing less number of carbon atoms than the original ketone.

(i) By strong oxidizing agents:

➤ The ketones are oxidized by strong oxidizing agents like con.  $\text{HNO}_3$ ,  $\text{KMnO}_4 / \text{H}_2\text{SO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}_2\text{SO}_4$  etc. and give mixture of carboxylic acids. Symmetrical ketones give mixture of two carboxylic acids. For example,



Unsymmetrical ketone gives mixture of four carboxylic acids. For example,

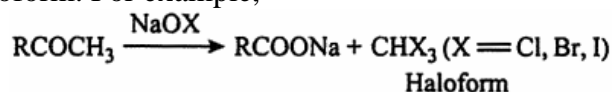


In case of unsymmetrical ketones, the keto group stays preferentially with the smaller alkyl group and is the main product and this is known as Popoff's rule.

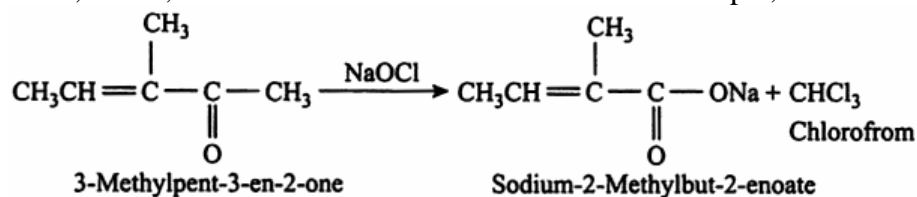


(ii) **Oxidation with sodium hypohalide (NaOX or X<sub>2</sub> + NaOH) (Iodoform test):**

➤ Aldehydes or ketones containing CH<sub>3</sub>CO-group, when treated with an excess of halogen in presence of alkali give haloform. For example,



During halo formation reaction, if carbon-carbon double bond is present in the molecules, the double bond is not oxidized; hence, double bond remains unaffected. For example,

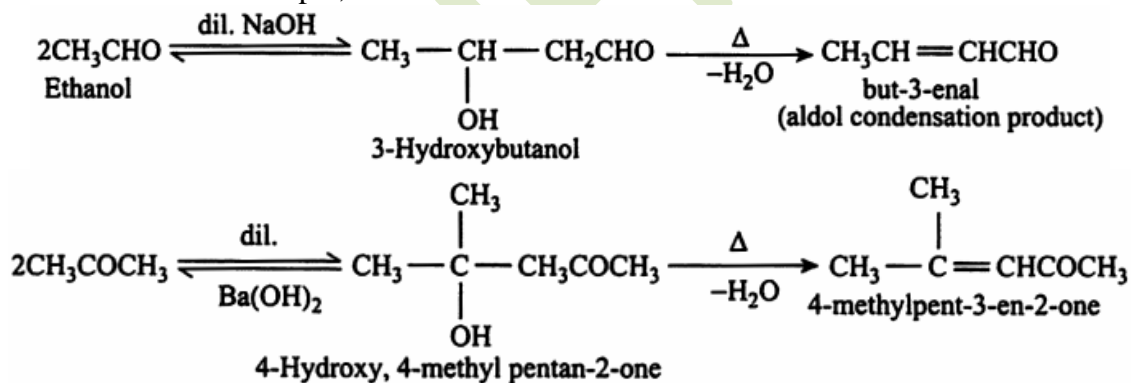


(9) **Explain aldol condensation.**

**Sol:** Due to acidity of α-hydrogen of aldehydes and ketones, they undergo a number of reactions such as aldol condensation, cross aldol condensation etc.

(i) **Aldol condensation:**

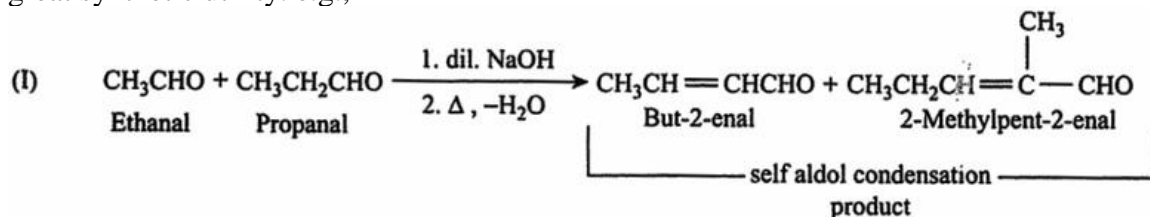
➤ In this reaction, two same molecules of an aldehyde or ketone, having at least one α-hydrogen atom undergo a reaction in presence of dilute alkali (dil. NaOH, Na<sub>2</sub>CO<sub>3</sub>, Ba(OH)<sub>2</sub> etc.) to form β-hydroxy aldehyde (Aldol) or β-hydroxy ketone (Ketol) respectively. This reaction is known as aldol condensation reaction. The name aldol is derived from the name of two functional groups aldehyde and alcohol present in the product. Same way ketol is derived from two functional groups of ketone and alcohol present in the product. The aldol and ketol readily lose water molecule to give α-β unsaturated carbonyl compounds which are aldol condensation product and the reaction is called aldol condensation. For example,

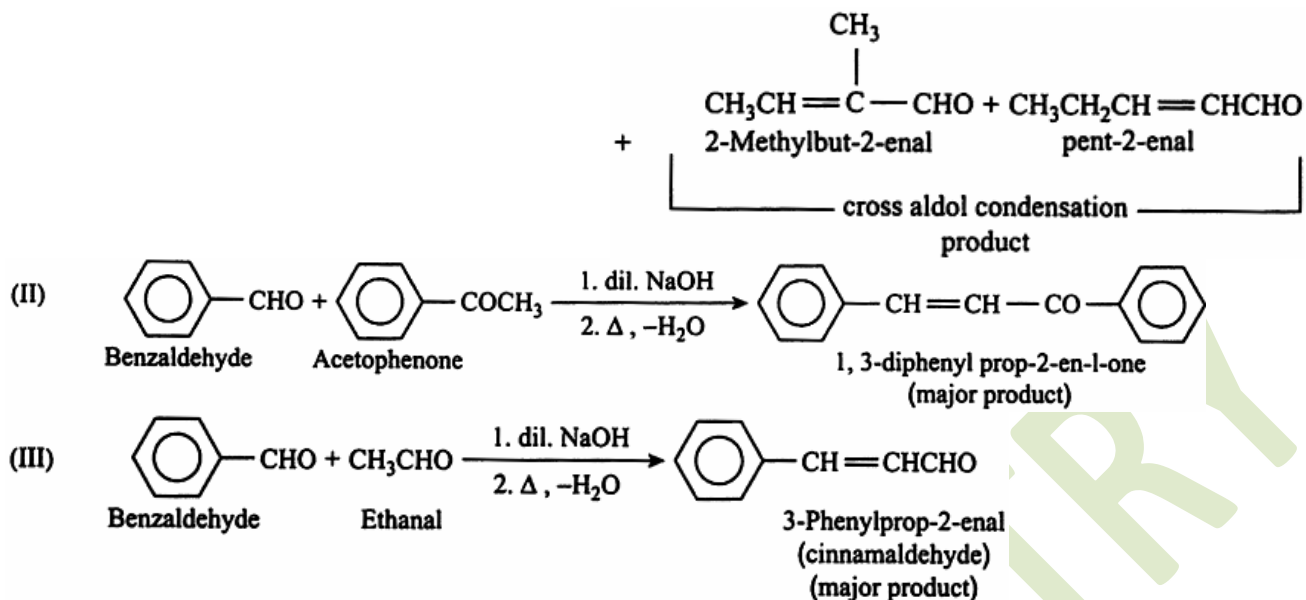


➤ Formaldehyde, benzaldehyde and benzophenone do not undergo aldol condensation since they do not have an α-hydrogen atom.

(10) **Explain: Cross-aldol condensation**

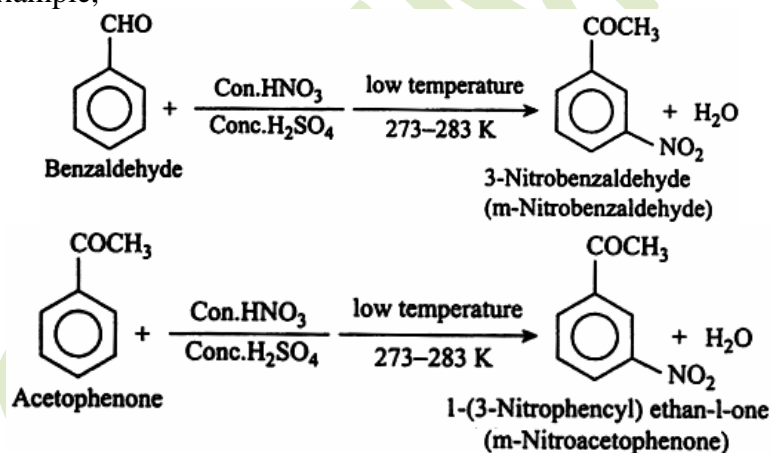
**Sol:** An aldol condensation between two different aldehydes or two different ketones or between one aldehyde and one ketone is called cross aldol condensation and gives mixture of four products which are difficult to separate. So cross aldol condensations are of little synthetic value. However, if one carbonyl compound does not possess α-hydrogen atom then cross aldol condensations are of great synthetic utility. e.g.,





(11) **Explain electrophilic substitution reactions of aromatic aldehydes and ketones.**

**Sol:** Electrophilic substitution reactions of aromatic aldehydes and ketones are as following:  
 Nitration: Aromatic aldehydes and ketones undergo electrophilic substitution reactions of the benzene nucleus. Since the aldehyde and ketone functional groups are electron withdrawing groups and so act as deactivating group and hence act as meta-directing group. So substitution occurs at meta position. For example,

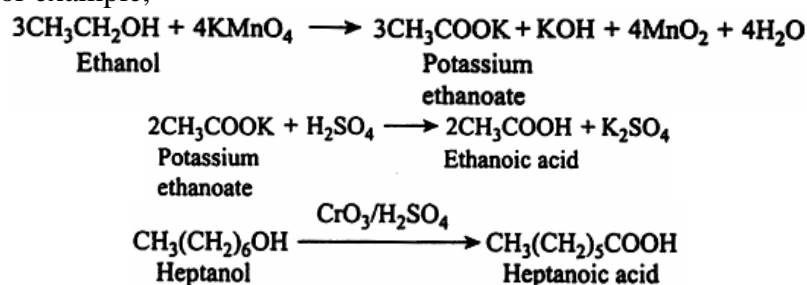


➤ Substitution reactions like halogenation, sulphonation also occur at m-position.

Give different methods for the preparation of carboxylic acid.

(12) **Explain: From primary alcohols and aldehydes**

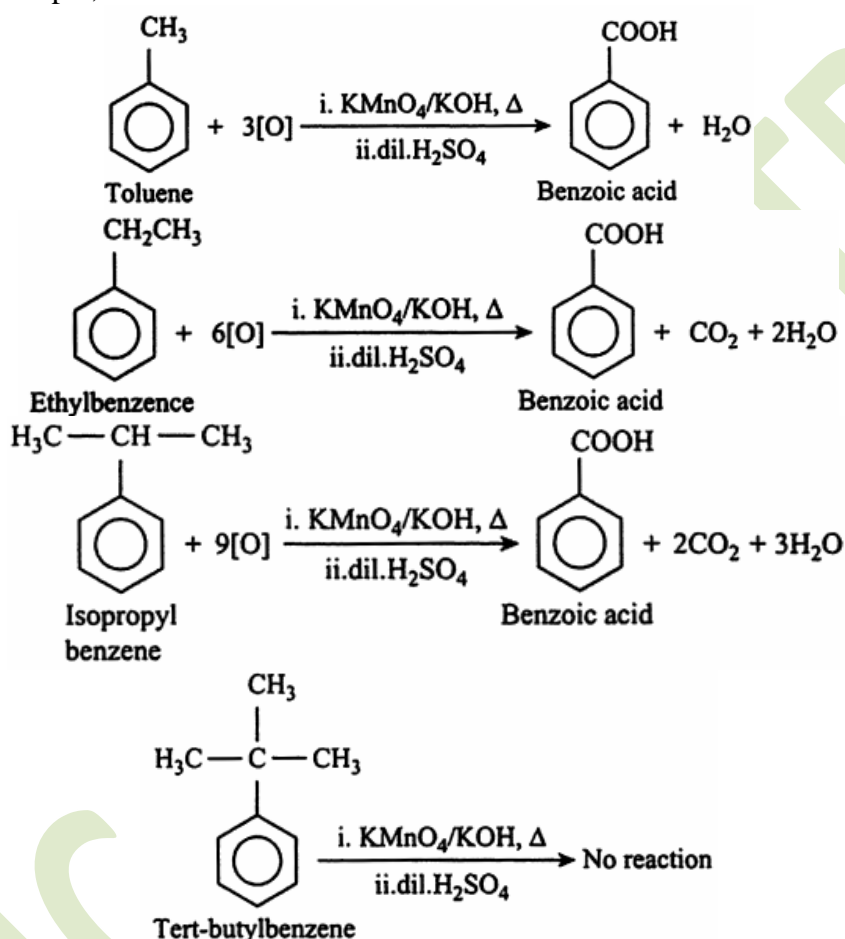
**Sol:** The primary alcohols are readily oxidized to the corresponding carboxylic acids with common oxidizing agents such as  $\text{KMnO}_4$  in neutral, acidic or alkaline medium or by  $\text{K}_2\text{Cr}_2\text{O}_7$  or  $\text{CrO}_3$  (chromium trioxide) in acidic medium oxidation with  $\text{K}_2\text{Cr}_2\text{O}_7$  or  $\text{CrO}_3$  in acidic medium often give some amount of esters. Therefore the oxidation with  $\text{KMnO}_4$  is preferred. Under these conditions the potassium salts of the carboxylic acids is first obtained, which on treatment with dilute  $\text{H}_2\text{SO}_4$  gives carboxylic acids. For example,



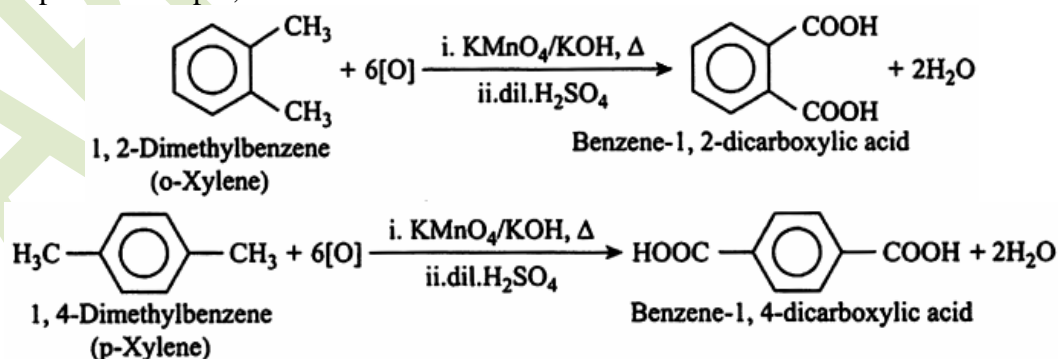
➤ Aldehydes are easily oxidized to corresponding carboxylic acids with  $\text{KMnO}_4$  in neutral, acidic or alkaline medium or by  $\text{K}_2\text{Cr}_2\text{O}_7$  or  $\text{CrO}_3$  in acidic medium and also even with mild oxidizing agent such as Tollen's reagent which is discussed in unit 5.4.

**(13) Explain: From alkylbenzene and alkenes**

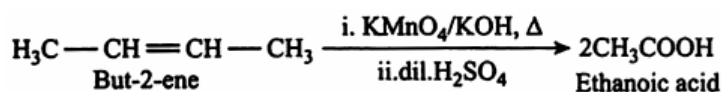
**Sol:** Aromatic carboxylic acids prepared by vigorous oxidation of alkylbenzene with acidic or alkaline  $\text{KMnO}_4$  or acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  (chromic acid) or dil.  $\text{HNO}_3$ . During these oxidation the entire side chain is oxidized to carboxylic acid group irrespective of the length of the side chain.  $1^\circ$  and  $2^\circ$  alkyl groups are oxidized in this manner but the  $3^\circ$  alkyl group is not oxidized and remains unaffected. For example,



➤ If there are two or more than two alkyl groups in benzene ring, each group is oxidized to  $-\text{COOH}$  group. For example,

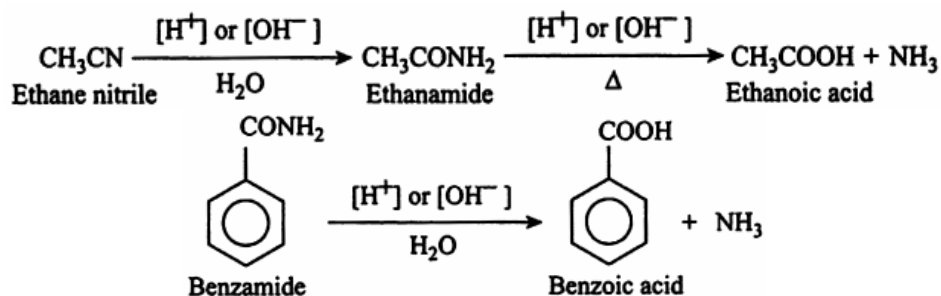


➤ Substituted alkenes are also oxidized to carboxylic acid by acidic  $\text{K}_2\text{Cr}_2\text{O}_7$  or alkaline  $\text{KMnO}_4$ . For example,



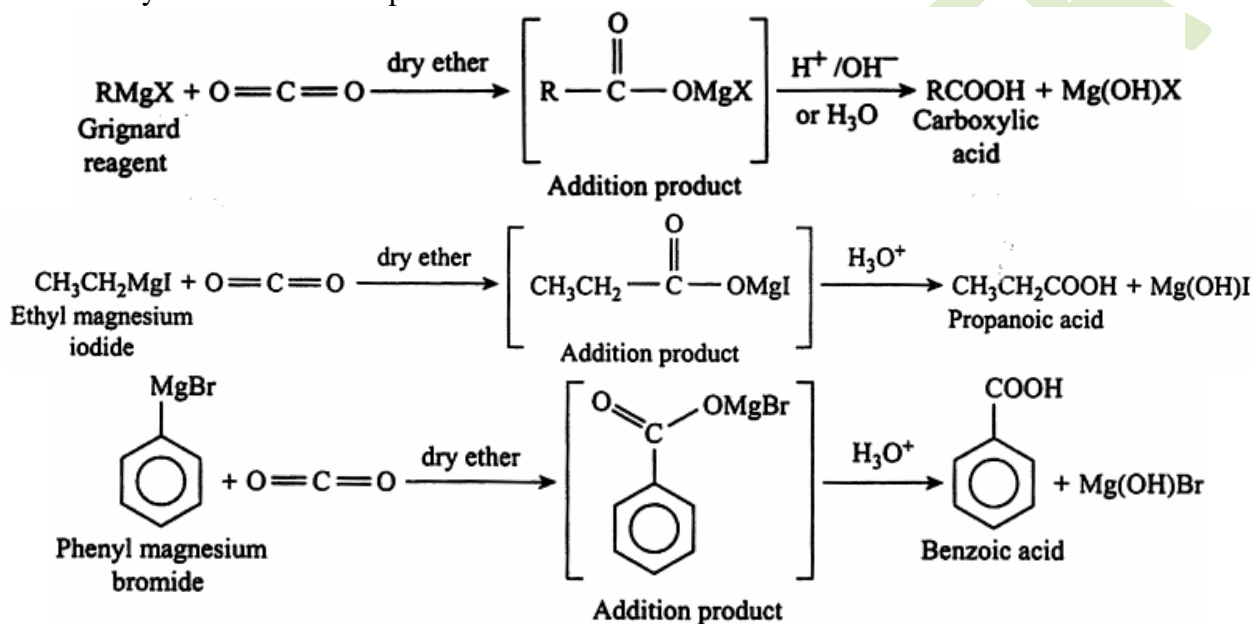
**(14) Explain: From nitriles and amines**

**Sol:** Nitriles are hydrolysed to amide and then to carboxylic acid on boiling with mineral acids or alkalis as a catalyst. For example,



(15) **Explain: From Grignard reagent**

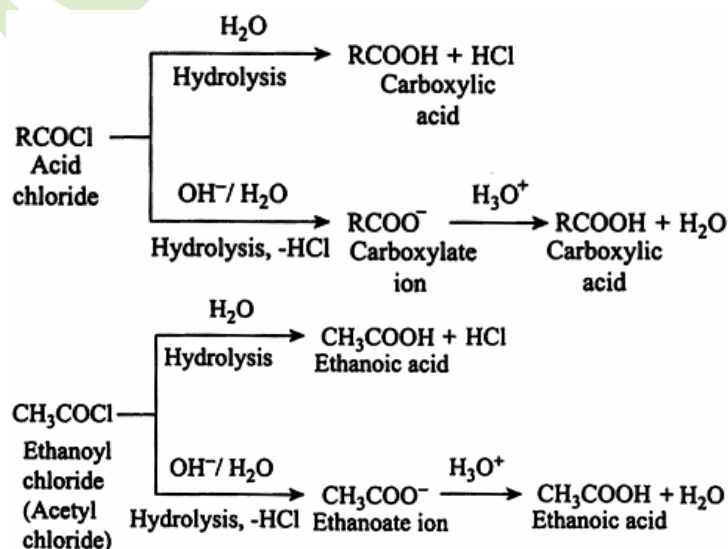
**Sol:** Carboxylic acids can be prepared by bubbling  $\text{CO}_2$  gas into ethereal solution of a suitable Grignard reagent or by adding the solution of Grignard reagent to crushed dry ice (solid  $\text{CO}_2$ ) suspended in ether. First the addition product is obtained, which on decomposition with mineral acid gives carboxylic acid. For example



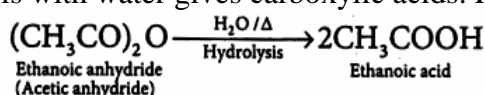
➤ In both the methods—nitriles and Grignard reagent are useful for converting the alkyl halide to the carboxylic acid, having carbon atom or atoms more than that present in alkyl halide.

(16) **Explain: From acid chloride and anhydrides**

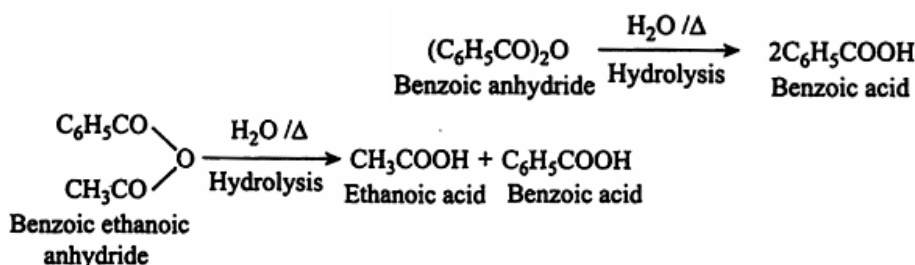
**Sol:** Acid chloride when hydrolysed by water gives carboxylic acid, and more readily hydrolyzed with aqueous alkali to give carboxylate ions, which on acidification gives corresponding carboxylic acids. For example,



- Anhydrides on hydrolysis with water give carboxylic acids. For example,
- Anhydrides on hydrolysis with water gives carboxylic acids. For example,

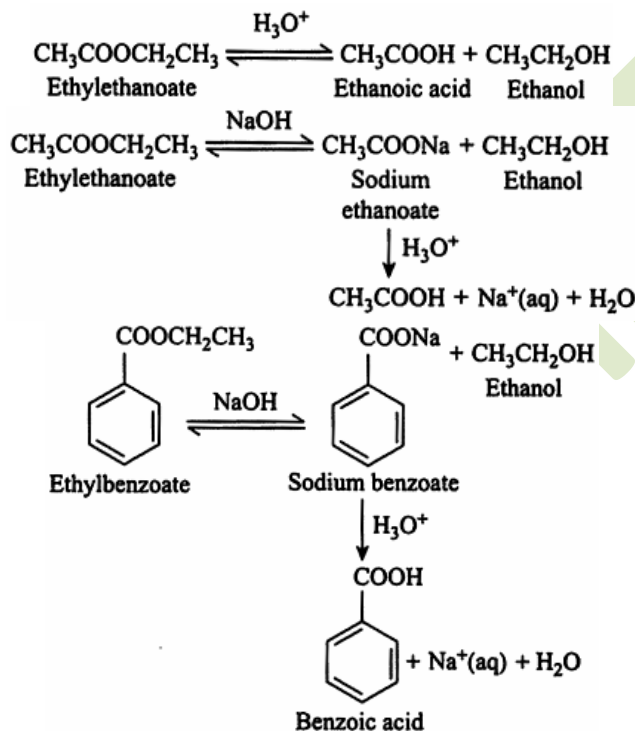






(17) Explain: From ester

**Sol:** Hydrolysis of ester in presence of mineral acids give carboxylic acids directly while hydrolysis in presence of alkali gives carboxylates, which on acidification give corresponding carboxylic acid for example,

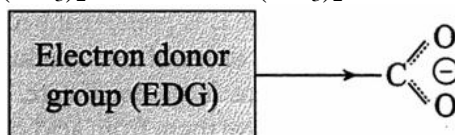


(18) Explain the factors that affect the acidic strength of carboxylic acids.

**Sol:** The acid strength of carboxylic acid depends on the effect of various substituents. For example,

(i) Effects on electron donating groups (EDG):

➤ The alkyl group has electron donating inductive effect (+I effect), hence it will increase the electron density in then -OH bond, so release of H<sup>+</sup> ions will be more difficult, hence formic acid is strongest acid than acetic acid. Further the +I effect of the alkyls group increases in the order CH<sub>3</sub><sup>-</sup> < CH<sub>3</sub>CH<sub>2</sub><sup>-</sup> < (CH<sub>3</sub>)<sub>2</sub>CH<sup>-</sup> < (CH<sub>3</sub>)<sub>3</sub>C<sup>-</sup> Hence the relative strength of carboxylic acid will be as CH<sub>3</sub>COOH > CH<sub>3</sub>CH<sub>2</sub>COOH > (CH<sub>3</sub>)<sub>2</sub>CHCOOH > (CH<sub>3</sub>)<sub>3</sub>COOH



(ii) Effects of electron withdrawing group (EWG):

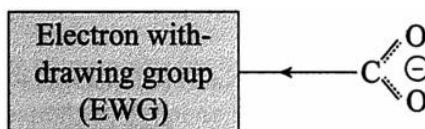
➤ Electron withdrawing group having -I effect, and it decreases in the order -F > -Cl > -Br > -I > -Ph. So the strength of the carboxylic acids will be as,

FCH<sub>2</sub>COOH > ClCH<sub>2</sub>COOH > BrCH<sub>2</sub>COOH > ICH<sub>2</sub>COOH > C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>COOH

Further, greater the number of electron withdrawing groups (Substituents), stronger will be the acid (strength)

Cl<sub>3</sub>CCOOH > Cl<sub>2</sub>CHCOOH > ClCH<sub>2</sub>COOH

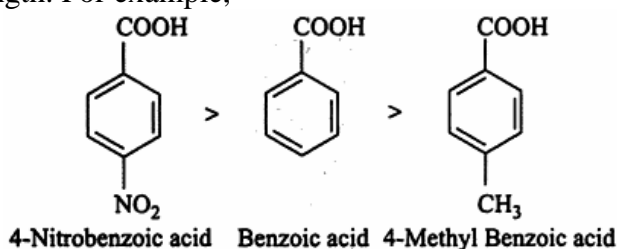
The inductive effect decreases rapidly with distance, so acidic strength order is CH<sub>3</sub>CH<sub>2</sub>CH(Cl)OOH > CH<sub>3</sub>CH(Cl)CH<sub>2</sub>COOH > ClH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COO



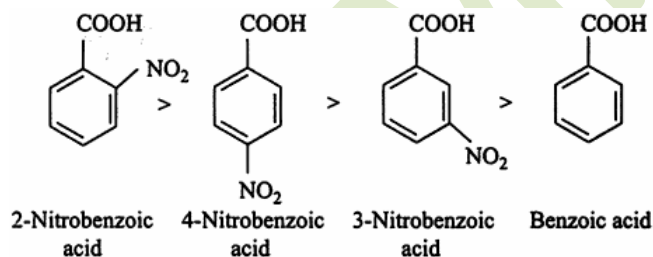
(iii) The phenyl or vinyl group directly attached to carboxyl group have weaker electron donating effect than alkyl group. So unsubstituted aromatic carboxylic acids are stronger acids than unsubstituted aliphatic carboxylic acids, but formic acid does not contain any alkyl group, therefore it is stronger acid than unsubstituted aromatic acid, so the order of acidic strength is

Formic acid > Benzoic acid > Acetic acid.

➤ For substituted aromatic carboxylic acid the presence of electron withdrawing group on the phenyl or aromatic carboxylic acid increases their acidic strength, while electron donating group, decreases their acidic strength. For example,



➤ Electron withdrawing or electron donating group effect is more pronounced at 1, 2 position (ortho position) than 1, 4 position (para position) than 1, 3 position (meta position). For example the acid strength is

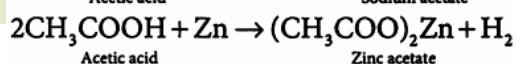
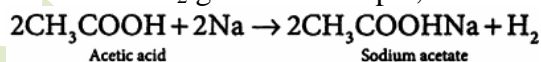


(19) Explain reaction involving cleavage of C–OH bond in carboxylic acid.

**Sol:** The reaction showing the acidic character of the carboxylic acid i.e. cleavage of O–H bond are given below:

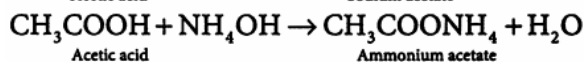
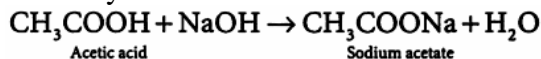
(i) **Reaction with metal:**

➤ Carboxylic acid like alcohols react with electropositive metals such as Na, K, Ca, Mg, Zn etc. to form their respective salts and liberate H<sub>2</sub> gas. For example,



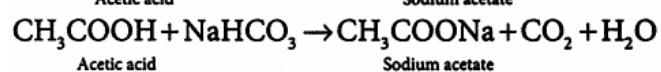
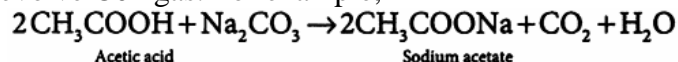
(ii) **Reaction with alkalis:**

➤ Similar to phenol the carboxylic acids neutralize alkalis and form salts. For example,



(iii) **Reaction with carbonates and hydrogen carbonates:**

➤ However unlike phenols the carboxylic acids react with weaker bases such as carbonates and hydrogen carbonates to evolve CO<sub>2</sub> gas. For example,

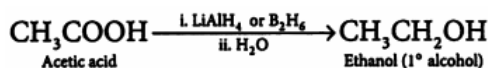


➤ This reaction is used to detect the presence of –COOH group in organic compounds. As most of the phenols do not produce CO<sub>2</sub> gas with NaHCO<sub>3</sub>. Hence this reaction is also useful to distinguish phenols from carboxylic acids.



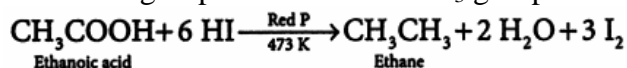
(24) **Explain: Reduction**

**Sol:** The reduction of carboxylic acids with Lithium aluminium hydride (LiAlH<sub>4</sub>) or better with diborane (B<sub>2</sub>H<sub>6</sub>) gives primary alcohol. Using this reaction the –CO– group can be reduced to –CH<sub>2</sub>– group. For example,



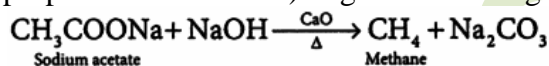
➤ Diborane does not easily reduce functional groups like ester, nitro, halo etc., and sodium borohydride does not reduce the carboxyl group.

➤ Carboxylic acid on reduction with hydrochloric acid and red phosphorus at 473 K gives alkanes. In this reaction the –COOH group is reduced to –CH<sub>3</sub> group.

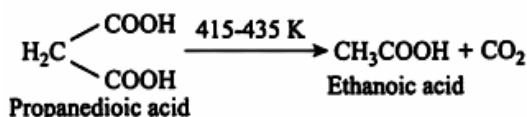


(25) **Explain: Decarboxylation**

**Sol:** Carboxylic acid and their salts lose carbon dioxide to form hydrocarbon and reaction is known as Decarboxylation reaction. The sodium salts of carboxylic acid are heated with sodalime (NaOH and CaO) mixture in proportion ratio of 3:1 to give alkane. e.g.,



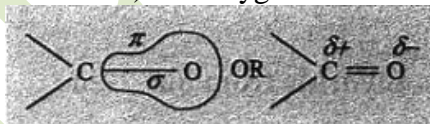
➤ If two carboxylic groups are attached to the same carbon atom called gem–di carboxylic acid undergo Decarboxylation simply on heating at 415–435 K temperature. For example,



➤ On electrolysis of aqueous solution of sodium or potassium salts of fatty acids at anode due to oxidation, CO<sub>2</sub> is liberated and alkane having double carbon is obtained. At cathode H<sub>2</sub> gas liberated and this process is called Kolbe's electrolytic reduction or electrolytic Decarboxylation.

(26) **Explain nature of carbonyl group.**

**Sol:** In carbonyl group the carbon–oxygen double bond is polarized due to higher electronegativity of oxygen atom relative to that of carbon atom. As a result the oxygen atom tends to attract the electron cloud of the π–bond towards itself as shown in figure. As a result the carbonyl carbon becomes an electrophile (Lewis acid) and oxygen becomes a nucleophile (Lewis base).



**Fig.** Electron cloud gets attracted more towards oxygen atom

➤ Thus the carbonyl group is polar in nature. Hence, such compounds have dipole moments. For example, aldehydes and ketones have 2.3–2.8 D dipole moment. The high polarity of the carbonyl group is explained on the basis of resonance structures shown below:

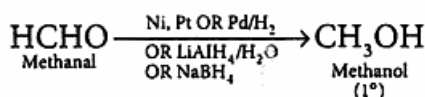


(27) **Explain reduction of aldehydes.**

**Sol:** Aldehydes on reduction forms either primary alcohol or hydrocarbon depending on the reaction condition.

(i) Reduction to alcohol:

➤ Aldehyde on reduction gives 1° alcohols. Reduction is carried out either catalytically with H<sub>2</sub> in presence of Ni, Pt or Pd or chemically Lithium aluminium hydride (LiAlH<sub>4</sub>) or sodium borohydride (NaBH<sub>4</sub>) LiAlH<sub>4</sub> is a much more powerful reducing agent than NaBH<sub>4</sub>.



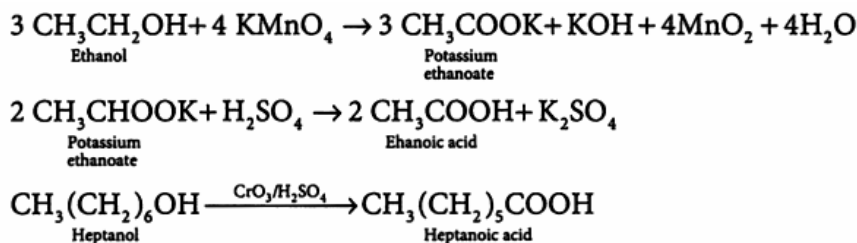
(ii) Reduction to hydrocarbon:

➤ The carbonyl group of aldehydes is reduced to methylene (–CH<sub>2</sub>–) group to form hydrocarbon by using different reducing agent.

(a) Wolff–Kishner reduction:

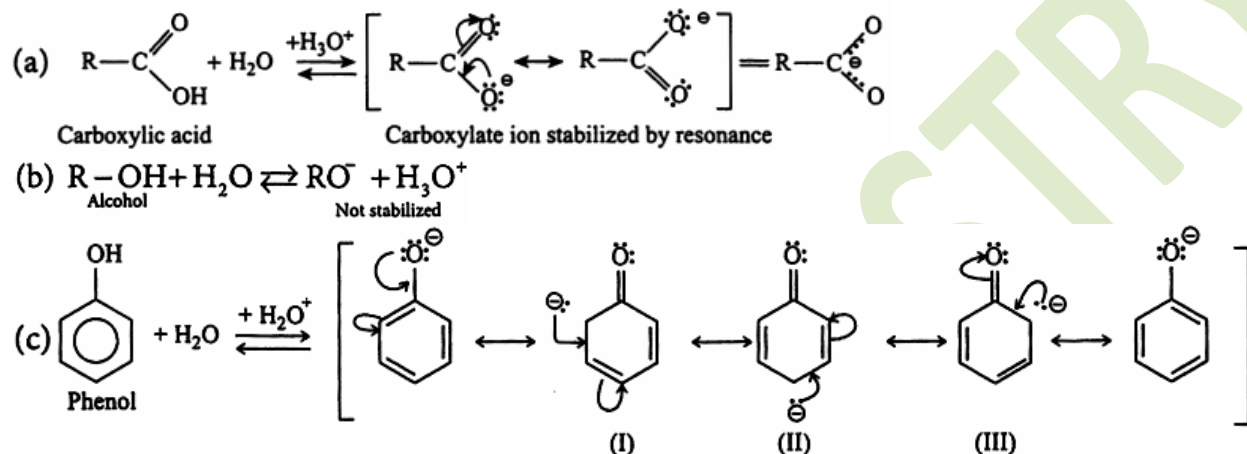






(32) Explain acidic nature of carboxylic acid.

**Sol:** Alcohols, phenols and carboxylic acids contain an -OH group, but the carboxylic acids are much stronger acid than alcohols and phenols. Comparison of acidic character of alcohols, phenols and carboxylic acids are based on the stability of resonance structure of their negative ions.



➤ As shown in reaction (a) carboxylate anions are stabilized by their resonance structures, so the tendency to release a proton is more, while the alkoxide ions as shown in reaction (b) are not stabilized by resonance, hence, alcohols have less tendency to release a proton, so alcohols are much weaker acids than carboxylic acids, though both contain an -OH group. In the case of phenoxide ions as shown in reaction (c) having resonance structures i to iii, but the structures carry a negative charge on the less electronegative carbon atoms.

➤ Therefore their contribution towards the resonance stabilization of phenoxide ion is very small, while in the carboxylate ion the negative charge is on the more electronegative oxygen atom, so carboxylic acids are stronger acids than alcohols and phenols. But they are weaker acids than mineral acids (HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>) and sulphonic acids.

➤ In aqueous solution, the carboxylic acid is ionized and exists in dynamic equilibrium between the carboxylate ion and the hydronium ion.



➤ So the equilibrium constant can be expressed

$$K_{\text{eq}} = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}][\text{H}_2\text{O}]} \quad \dots \text{eq. 1}$$

➤ Since water is taken in large excess, hence [H<sub>2</sub>O] remains constant, so the equation can be written as

$$K_{\text{eq}} \times [\text{H}_2\text{O}] = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]} = K_a \quad \dots \text{eq. 2}$$

➤ The equilibrium constant K<sub>a</sub> is called the dissociation constant of the acid, and it varies with the temperature for a given acid. From equation (2) it is clear that at constant temperature K<sub>a</sub> is directly proportional to the [H<sub>3</sub>O<sup>+</sup>]. Therefore the value K<sub>a</sub> is a measure of the acid strength of an acid, so the higher the value of K<sub>a</sub>, the greater is the tendency of the acid to ionize and hence stronger is the acid. For convenience, the strength of an acid is generally indicated by its pK<sub>a</sub> value, rather than its K<sub>a</sub> value

$$\text{pK}_a = -\log k_a$$

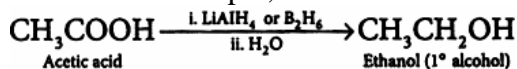
➤ So, if a carboxylic acid has a smaller numerical value of pK<sub>a</sub>, then it is very strong, i.e. better proton donor. Strong acids have pK<sub>a</sub> values < 1, the acids with pK<sub>a</sub> values between 1 and 5 are

considered to be moderately strong acids, weak acids have  $pK_a$  values between 5 and 15 extremely weak acid have  $pK_a$  value  $>15$ .

**(33) Explain reduction of acetic acid.**

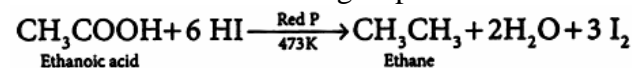
**Sol:** The reduction of acetic acid with lithium aluminium hydride ( $LiAlH_4$ ) or better with diborane ( $B_2H_6$ ) gives primary alcohol. Using this reaction the  $-CO-$  group can be reduced to  $-CH_2-$  group.

➤ For example,



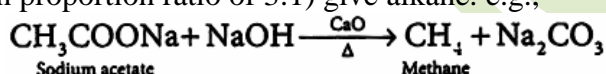
➤ Diborane does not easily reduce functional groups like ester, nitro, halo etc., and sodium borohydride does not reduce the carboxyl group.

➤ Acetic acid on reduction with hydrochloric acid and red phosphorus at 473K give alkanes. In this reaction the  $-COOH$  group is reduced to  $-CH_3$  group.

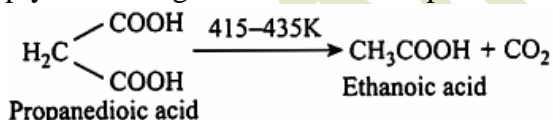


**(34) Explain decarboxylation.**

**Sol:** Carboxylic acid and their salts lose carbon dioxide to form hydrocarbon and reaction is known as Decarboxylation reaction. The sodium salt of carboxylic acid are heated with sodalime ( $NaOH$  and  $CaO$  mixture in proportion ratio of 3:1) give alkane. e.g.,



➤ If two carboxylic groups are attached to the same carbon atom called gem-di carboxylic acid undergo decarboxylation simply on heating at 415–435 K temperature. For example,

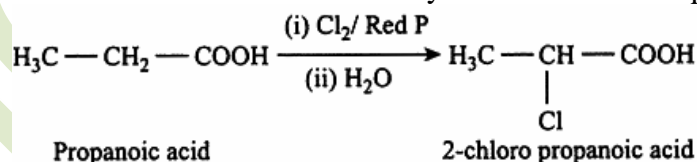


➤ On electrolysis of aqueous solution of sodium or potassium salts of fatty acids at anode due to oxidation,  $CO_2$  is liberated and alkane having double carbon is obtained. At cathode  $H_2$  gas liberated and this process is called Kolbe's electrolytic reduction or electrolytic Decarboxylation.

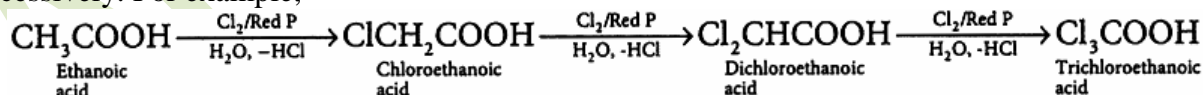
**(34) Explain halogenation of acetic acid.**

**Sol:** Carboxylic acid having an  $\alpha$ -hydrogen atoms are halogenated at the  $\alpha$ -position on treatment with dichlorine or dibromine in the presence of small amount of red phosphorous to give  $\alpha$ -halocarboxylic acid.

➤ This reaction is known as Hell Volhard Zelin-sky reaction. For example,



➤ If more than one mole of  $Cl_2$  or  $Br_2$  are used then the 2<sup>nd</sup> and 3<sup>rd</sup>  $\alpha$ -hydrogen atoms are successively. For example,

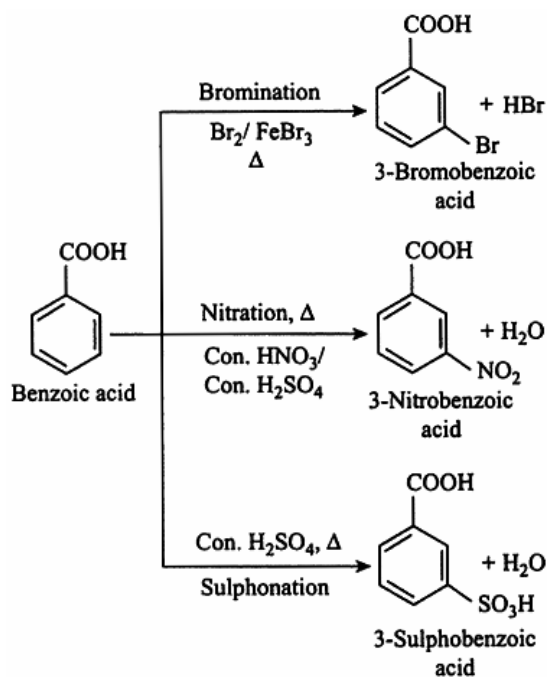


**(35) Explain ring substitution of benzoic acid.**

**Sol:** Aromatic carboxylic acids undergo the electrophilic substitution reaction like halogenation, nitration and sulphonation.

➤ Since  $-COOH$  groups acts as a deactivating and hence m-directing group, so the reactions take place only under vigorous conditions.

➤ The  $-COOH$  group deactivates the benzene ring and catalyst aluminium chloride (Lewis acid) gets bonded to the carbonyl group. So they do not undergo Friedel-Crafts reaction.



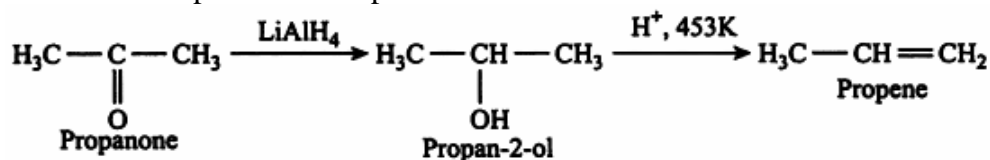
(36) Give IUPAC names: (Any Two)

Sol:

| Structure   | IUPAC name                          |
|---|-------------------------------------|
| $\begin{array}{ccccccc} \text{H}_3\text{C} & - & \text{CH} & - & \text{CH}_2 & - & \text{CH} & - & \text{COOH} \\ & &   & & & &   & & \\ & & \text{Cl} & & & & \text{NO}_2 & & \end{array}$   | 4-Chloro-2-nitropentanoic acid      |
| $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$  | Butane nitrile                      |
| $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$   | Ethyl propanoate                    |
|   | 3-Bromo-5-chlorobenzoic acid        |
|   | Benzene 1,3-dicarboxylic acid       |
| $\begin{array}{ccccccc} \text{H}_3\text{C} & - & \text{CH} & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CHO} \\ & &   & & & & & & \\ & & \text{Br} & & & & & & \end{array}$  | 4-Bromo pentanal                    |
| $\begin{array}{ccccccc} \text{H}_3\text{C} & - & \text{CH}_2 & - & \text{CH} & - & \text{CO} & - & \text{CH}_2 & - & \text{CH}_3 \\ & & & &   & & & & & & \\ & & & & \text{Cl} & & & & & & \end{array}$   | 4-Chlorohexan-3-one                 |
| $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$  | Pentan-2-one                        |
| $\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{COOH}$  | Pentanedioic acid                   |
| $\begin{array}{ccccccc} \text{H}_3\text{C} & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH} & - & \text{CH}_2 & - & \text{CH}_3 \\ & & & & & &   & & & & \\ & & & & & & \text{COOH} & & & & \end{array}$   | 2-Ethyl pentanoic acid              |
| $\begin{array}{ccccccc} & & & & \text{COOH} & & & & & & \\ & & & &   & & & & & & \\ \text{H}_3\text{C} & - & \text{CH}_2 & - & \text{CH} & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{COOH} \end{array}$   | 2-Ethyl pentanedioic acid           |
| $\begin{array}{ccccccc} & & & & \text{COOH} & & & & & & \\ & & & &   & & & & & & \\ \text{H}_3\text{C} & - & \text{CH} & - & \text{CH} & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{COOH} \\ & & & &   & & & & & & \\ & & & & \text{COOH} & & & & & & \end{array}$ | Pentane-1,3, 4-tricarboxylic acid   |
| $\text{H}_3\text{C}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{COOH}$  | Hex-3-enoic acid                    |
| $\begin{array}{ccccccc} \text{H}_3\text{C} & - & \text{CH}_2 & - & \text{CH} & - & \text{CH} & - & \text{CH} & - & \text{CO} & - & \text{CH}_3 \\ & & & &   & &   & &   & & & & \\ & & & & \text{Cl} & & \text{Br} & & \text{I} & & & & \end{array}$                  | 4-Bromo-5-chloro-3-iodoheptan-2-one |

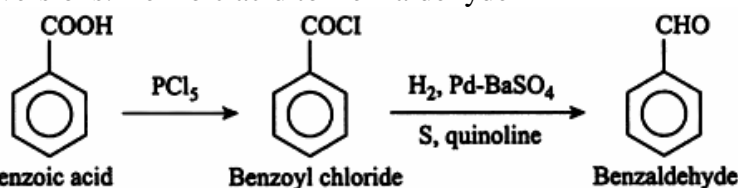


(37) Give conversions: Propanone to Propene



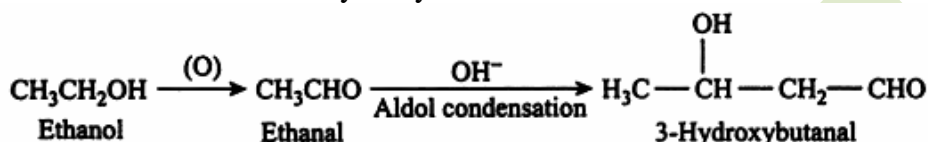
Sol:

(38) Give conversions: Benzoic acid to Benzaldehyde



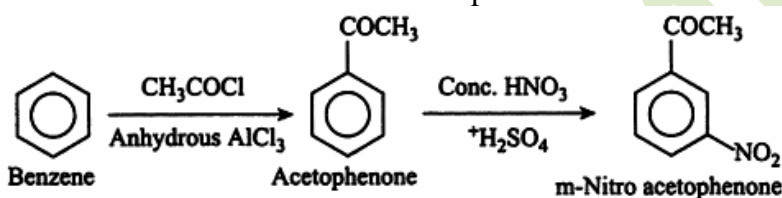
Sol:

(39) Give conversions: Ethanol to 3-Hydroxybutanal



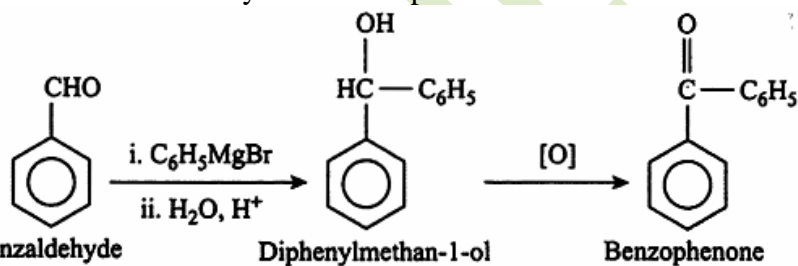
Sol:

(40) Give conversions: Benzene to m-Nitroacetophenone



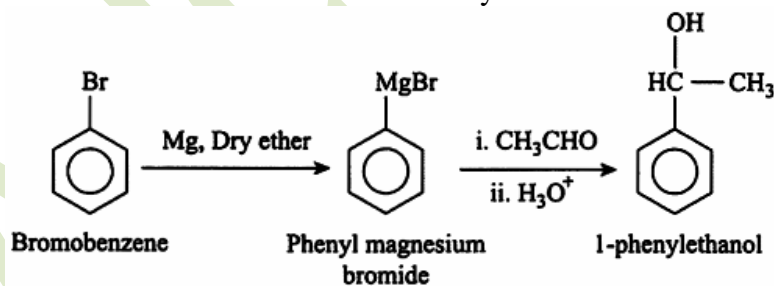
Sol:

(41) Give conversions: Benzaldehyde to Benzophenone



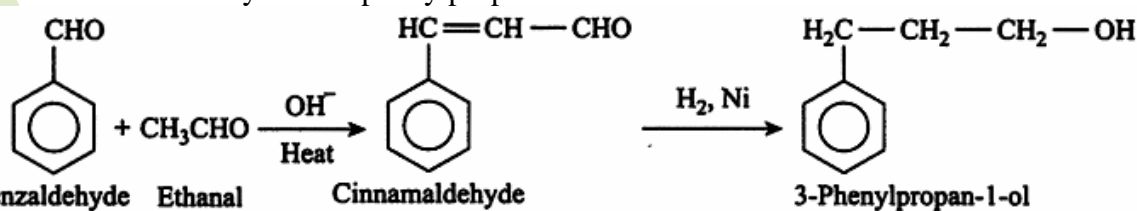
Sol:

(42) Give conversions: Bromobenzene to 1-Phenylethanol



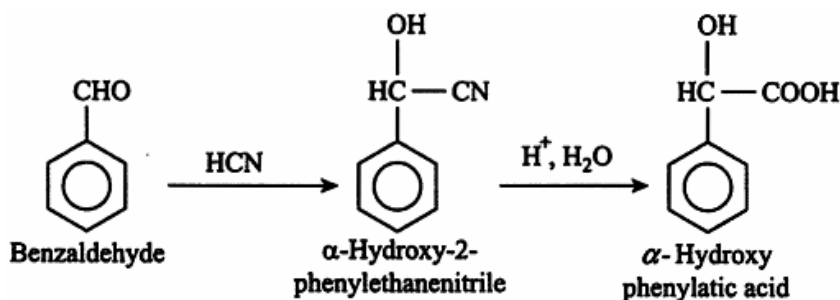
Sol:

(43) Give conversions: Benzaldehyde to 3-phenylpropan-1-ol



Sol:

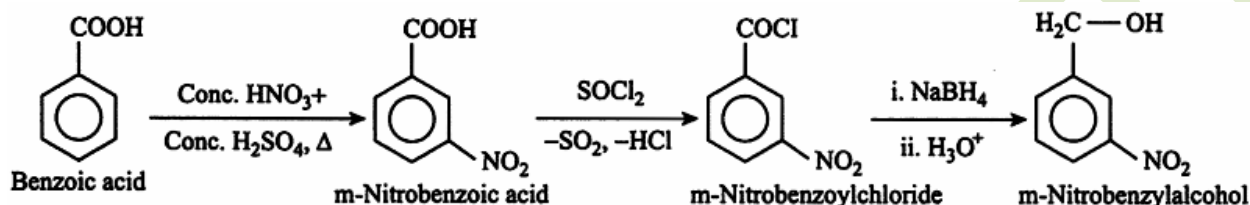
(44) Give conversions: Benzaldehyde to  $\alpha$ -Hydroxyphenylacetic acid



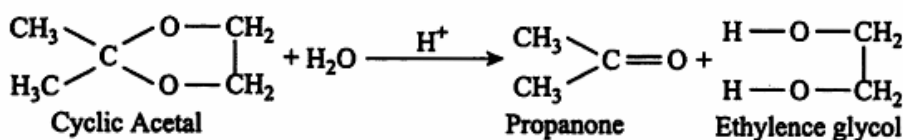
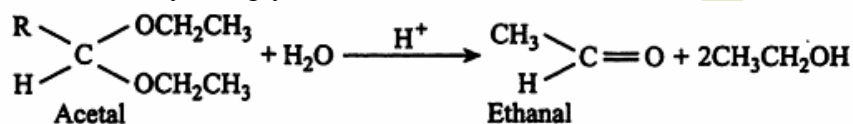
Sol:

(45) Give conversions: Benzoic acid to m-Nitrobenzyl alcohol

Sol:

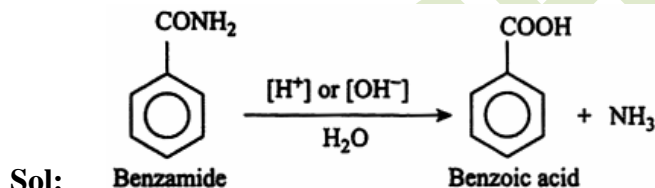


(46) Give conversions: Ethylene glycol from acetal

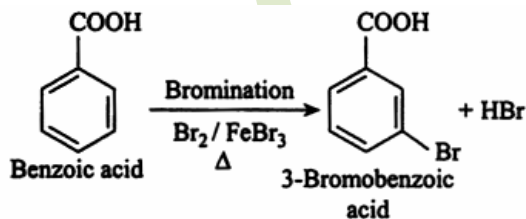


Sol:

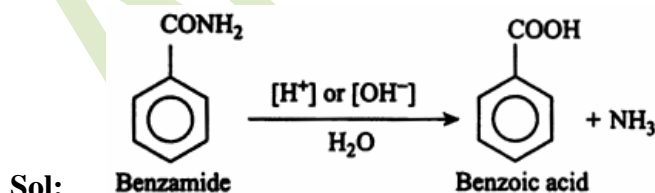
(47) Give conversions: 3-Bromobenzoic acid from benzamide.



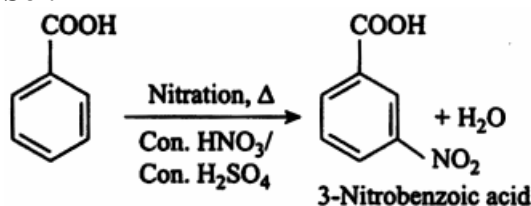
Sol:



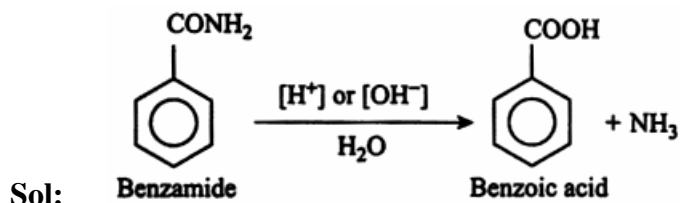
(48) Give conversions: 3-Nitrobenzoic acid from benzamide.



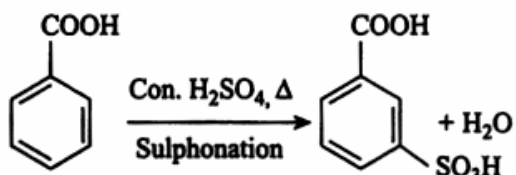
Sol:



(49) Give conversions: 3-sulphobenzoic acid from benzamide.



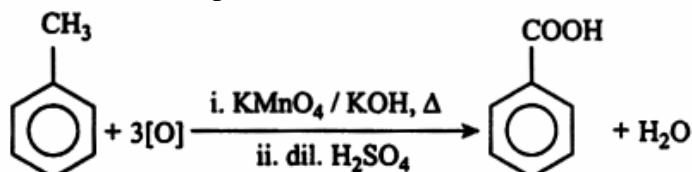
Sol: Benzamide



Sol: Benzoic acid

3-Sulphobenzoic acid

(50) Give conversions: 3-sulphobenzoic acid from toluene.

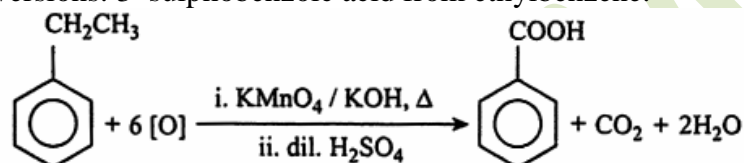


Sol: Toluene

Benzoic acid

For second step, refer second step of 13<sup>th</sup> conversion.

(51) Give conversions: 3-sulphobenzoic acid from ethylbenzene.

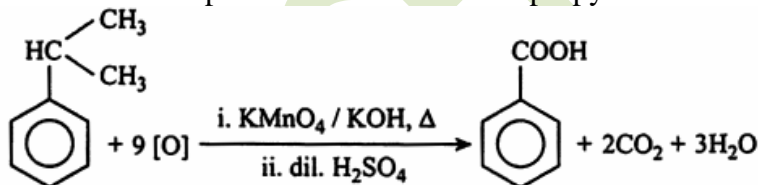


Sol: Ethylbenzene

Benzoic acid

For second step, refer second step of 13<sup>th</sup> conversion.

(52) Give conversions: 3-sulphobenzoic acid from isopropyl benzene.

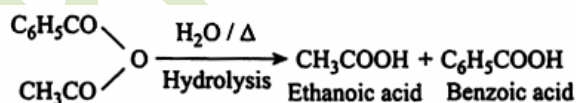


Sol: Isopropyl benzene

Benzoic acid

For second step, refer second step of 13<sup>th</sup> conversion.

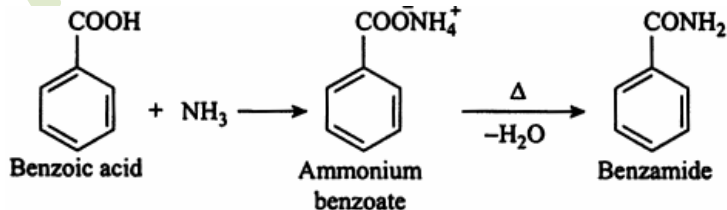
(53) Give conversions: 3-Bromobenzoic acid from benzoic ethanoic anhydride



Sol: Benzoic ethanoic anhydride

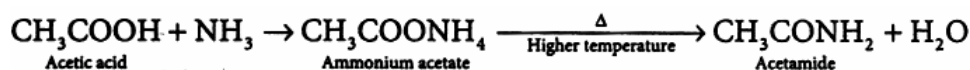
For second step, refer second step of 11<sup>th</sup> conversion.

(54) Give conversions: Benzamide from benzoic acid



Sol:

(55) Give conversions: Acetamide from acetic acid



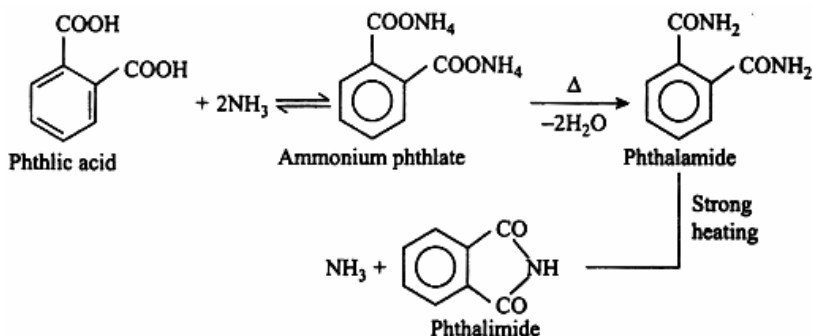
Sol:

Acetic acid

Ammonium acetate

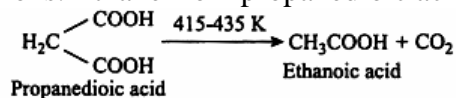
Acetamide

(56) Give conversions: Phthalimide from phthalic acid



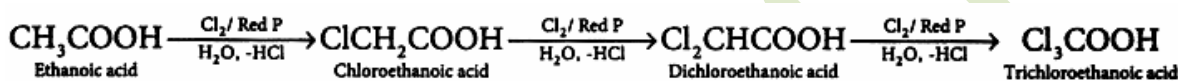
**Sol:**

- (57) Give conversions: Ethane from propanedioic acid



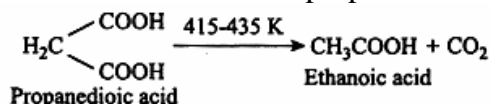
**Sol:**

- (58) Give conversions: Trichloro/dichloro ethanoic acid from ethanoic acid



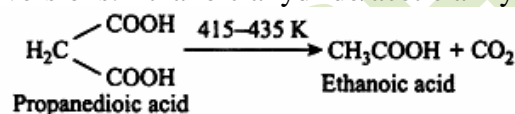
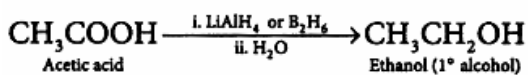
**Sol:**

- (59) Give conversions: Ethanol from propanedioic acid



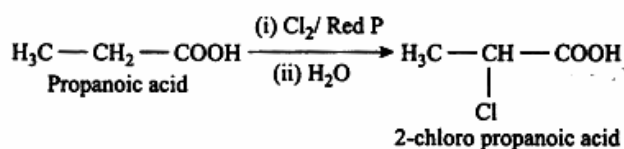
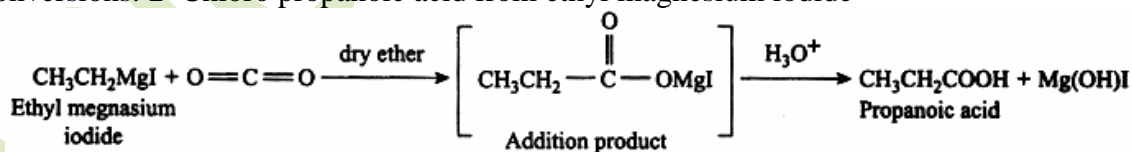
**Sol:**

- (60) Give conversions: Ethanoic anhydride/acetic anhydride from propanedioic acid



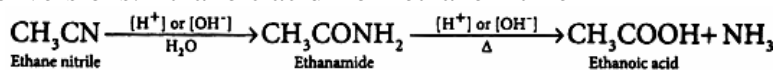
**Sol:**

- (61) Give conversions: 2-Chloro propanoic acid from ethyl magnesium iodide



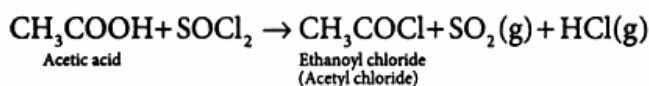
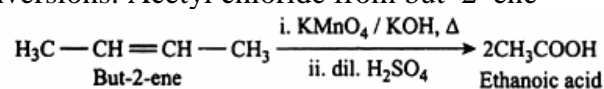
**Sol:**

- (62) Give conversions: Ethanoic acid from ethane nitrile



**Sol:**

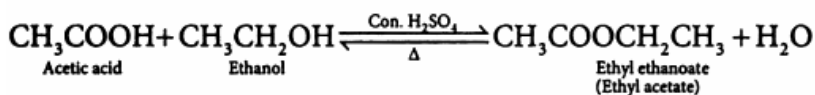
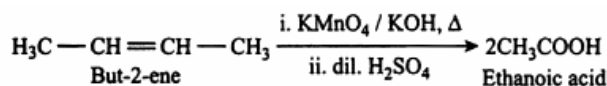
- (63) Give conversions: Acetyl chloride from but-2-ene



**Sol:**

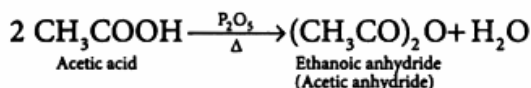
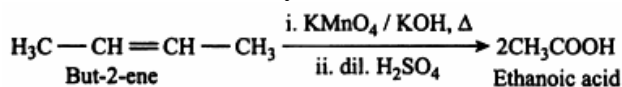
- (64) Give conversions: Ethyl ethanoate from but-2-ene





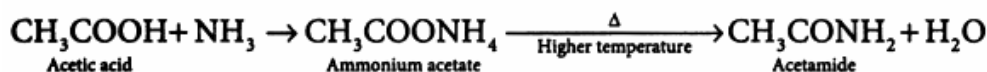
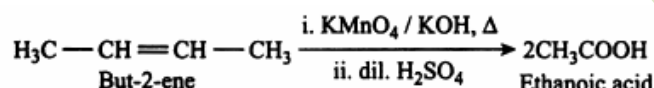
Sol:

- (65) Give conversions: Acetic anhydride from but-2-ene



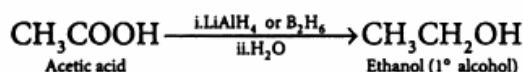
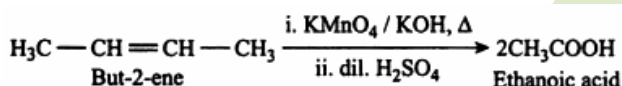
Sol:

- (66) Give conversions: Acetamide from but-2-ene



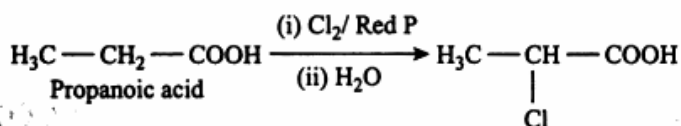
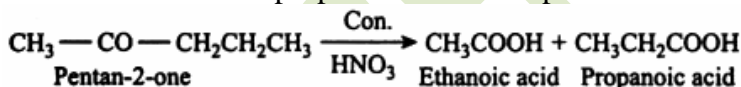
Sol:

- (67) Give conversions: Ethanol from but-2-ene



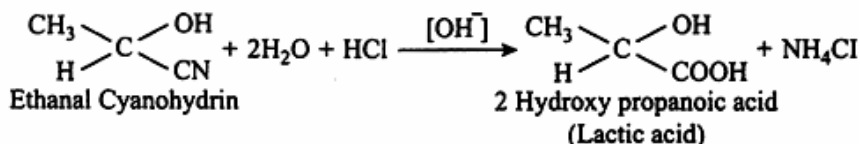
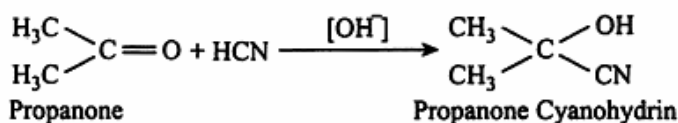
Sol:

- (68) Give conversions: 2-Chloro propanoic acid from pentan-2-one



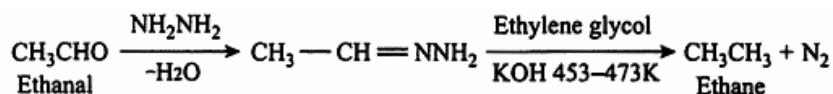
Sol:

- (69) Give conversions: Lactic acid from propanone.



Sol:

- (70) Give conversions: Ethane from ethanal



Sol: