

Aldehydes, Ketones and Carboxylic Acids

CHAPTER 8



ANSWERS

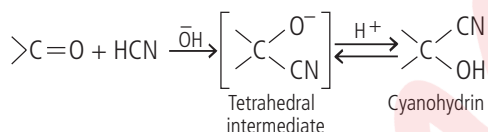
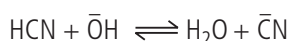
Topic 1

1.

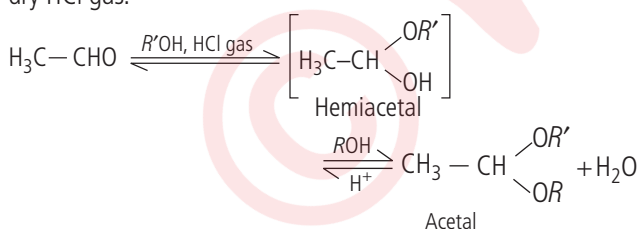
IUPAC name	Common name
(i) Heptan-2-one	Methyl- <i>n</i> -pentylketone
(ii) 4-Bromo-2-methylhexanal	γ -Bromo- α -methyl caproaldehyde
(iii) Heptanal	Heptanaldehyde
(iv) 3-Phenylprop-2-enal	β -Phenylacrolein
(v) Cyclopentane carbaldehyde	—
(vi) Diphenylmethanone	Benzophenone

Topic 2

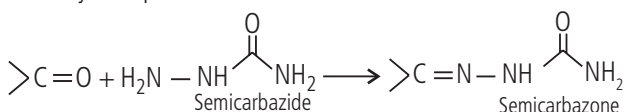
1. (i) Carbonyl compounds in the presence of an alkali, react with HCN to form an addition product called cyanohydrin.



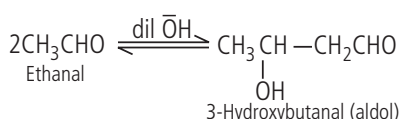
(ii) Acetals are *gem*-dialkoxy compounds formed when aldehydes react with monohydric alcohols in the presence of dry HCl gas.



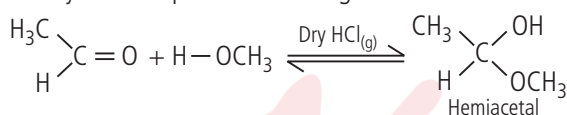
(iii) Semicarbazone is formed by the reaction between carbonyl compounds and semicarbazide.



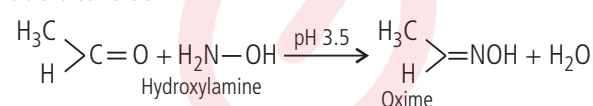
(iv) β -Hydroxy aldehydes are called aldol. Aldehydes and ketones containing at least one α -H atom undergo a reaction in the presence of dilute alkali to form aldol compounds. *e.g.*,



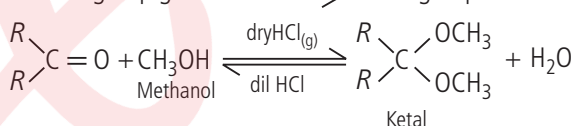
(v) Hemiacetals are *gem*-alkoxyalcohols which are produced from the addition of one molecule of monohydric alcohol to an aldehyde in the presence of HCl gas.



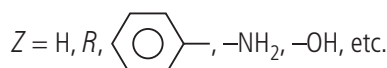
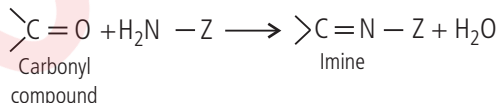
(vi) Oximes are formed by reaction between aldehydes or ketones and hydroxylamine. The reaction is carried out in mildly acidic condition.



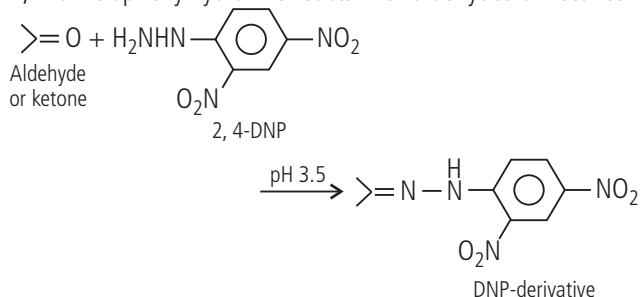
(vii) Ketals are obtained when alcohols react with ketone and two OR group get attached to $>\text{C}=\text{O}$ group of ketone.



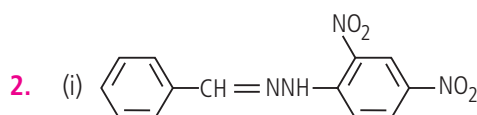
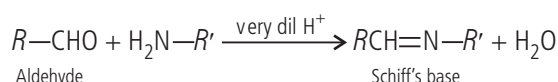
(viii) Imines are formed when carbonyl compounds react with ammonia and its derivatives.

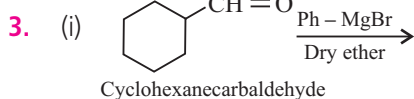
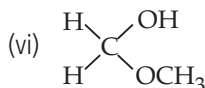
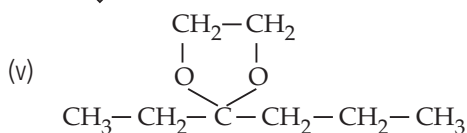
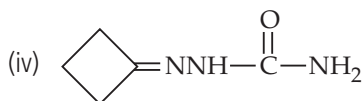
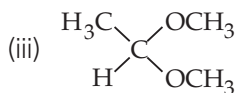
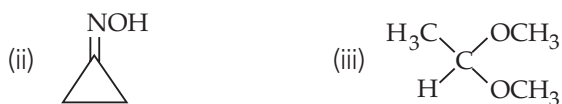


(ix) 2, 4-DNP derivatives are formed when 2, 4-dinitrophenylhydrazine reacts with aldehydes or ketones.

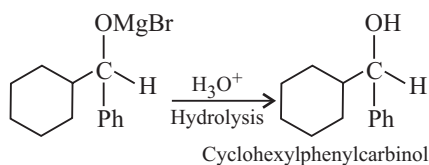


(x) Reaction between aldehydes or ketones with 1° aliphatic or aromatic amines yields a Schiff's base.

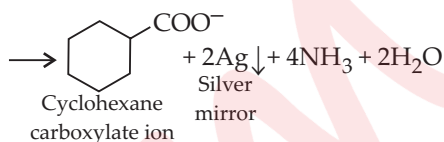
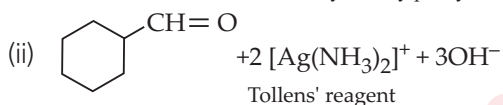




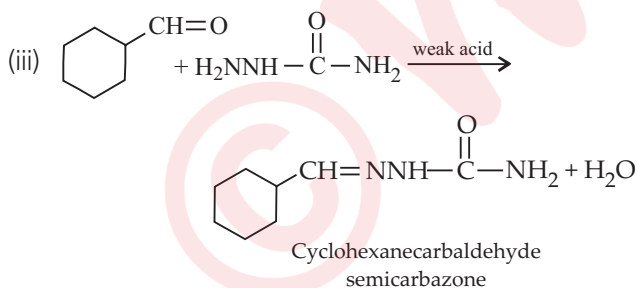
Cyclohexanecarbaldehyde



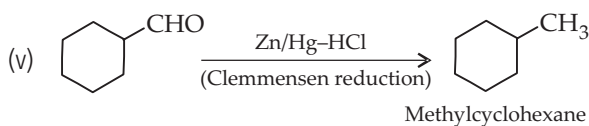
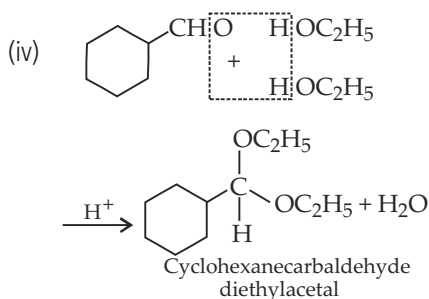
Cyclohexylphenylcarbinol



Cyclohexane carboxylate ion



Cyclohexanecarbaldehyde semicarbazone

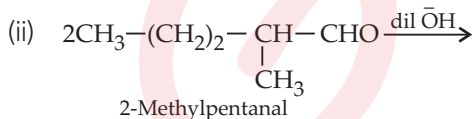


4. Aldol condensation is shown by those aldehydes or ketones which have at least one α -H atom while Cannizzaro reaction is shown by aldehydes that have no α -H atom.

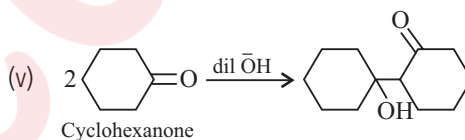
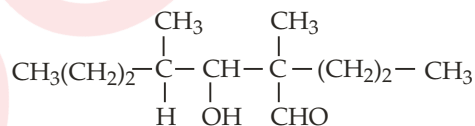
Therefore, the given compounds can be classified as:

Aldol Condensation	Cannizzaro Condensation	Neither Aldol nor Cannizzaro
2-Methylpentanal	Methanal	Butan-1-ol
Cyclohexanone	Benzaldehyde	Benzophenone
1-Phenylpropanone	2, 2-Dimethylbutanal	
Phenylacetaldehyde		

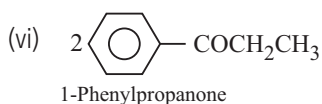
Aldol condensations :



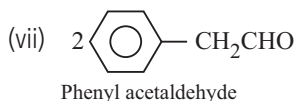
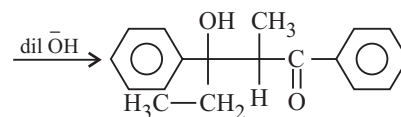
2-Methylpentanal



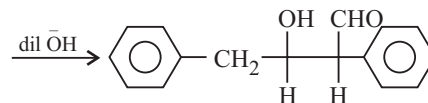
Cyclohexanone



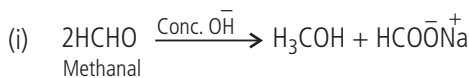
1-Phenylpropanone



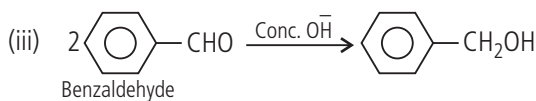
Phenyl acetaldehyde



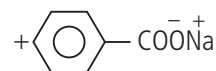
Cannizzaro reactions :

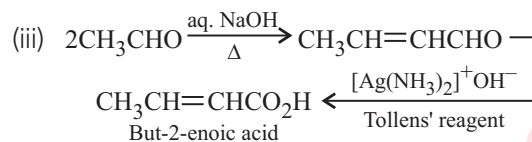
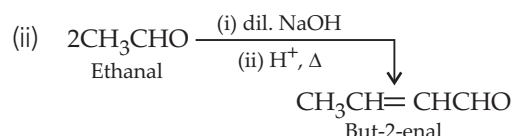
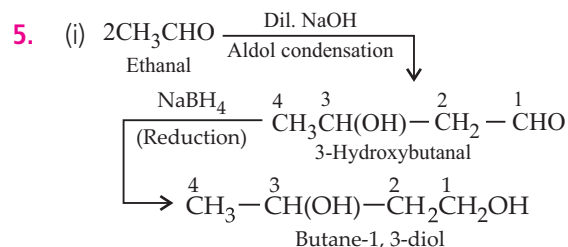
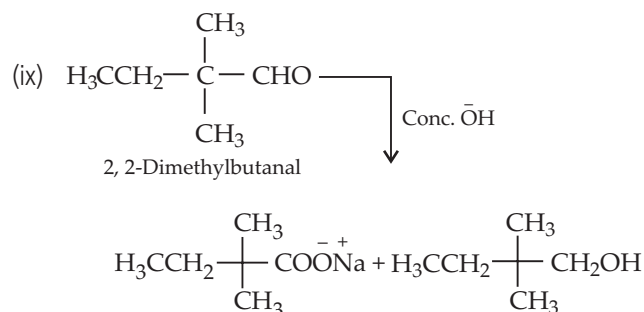


Methanal

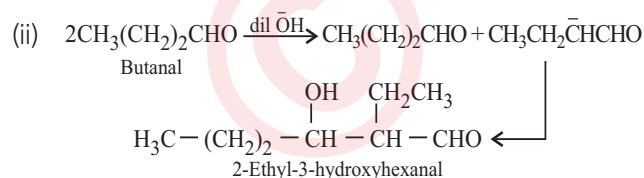
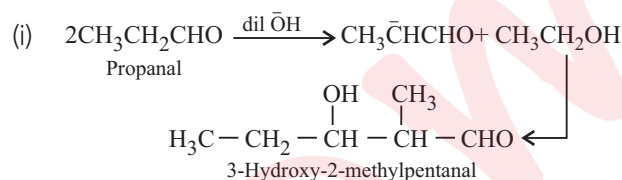


Benzaldehyde

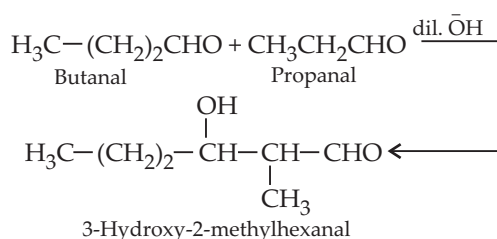




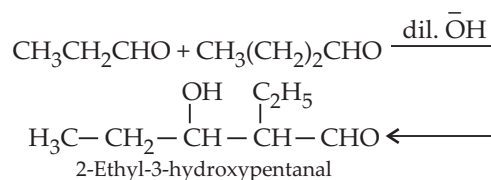
6. The possible products of aldol condensation from propanal and butanal are



(iii) When butanal acts as an electrophile and propanal as nucleophile :



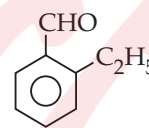
(iv) When propanal serves as an electrophile and butanal as nucleophile :



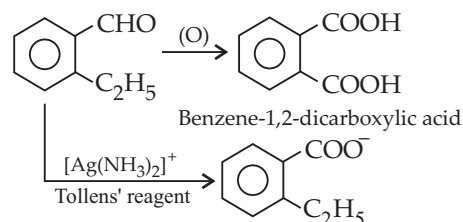
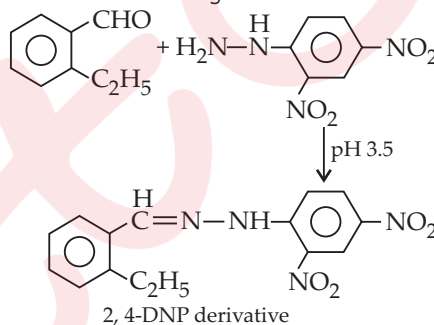
7. (i) It is given that the compound reduces Tollens' reagent. This proves that the compound is an aldehyde. Further, the fact that it undergoes Cannizzaro reaction shows that it lacks an α -H atom.

(ii) On oxidation it yields 1,2-benzenedicarboxylic acid. This shows that it is an *o*-substituted benzaldehyde.

The only possible structure for the compound with formula $\text{C}_9\text{H}_{10}\text{O}$ is :



The reactions undergone are :



8. (a) The given compound does not reduce Tollens' reagent which implies that it is not an aldehyde.

(b) Positive iodoform test proves that it has a $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-$ group.

(c) The oxidation products are indicative of the presence of 5 carbon atoms.

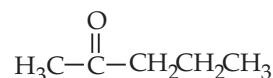
To find the exact molecular formula

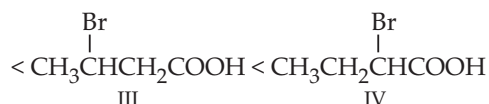
$$\% \text{C} = 69.77\%, \% \text{H} = 11.63\%$$

$$\% \text{O} = 100 - (69.77 + 11.63) = 18.6 \%$$

$$\text{C} : \text{H} : \text{O} = \frac{69.77}{12} : \frac{11.63}{1} : \frac{18.6}{16}$$

The structure based on inferences a, b and c is

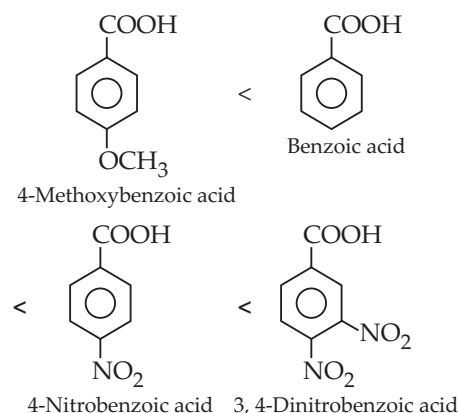




Between I and II the higher acidity of II is due to lesser number of $-\text{CH}_3$ groups on the α -carbon. $-\text{CH}_3$ group increases the electron density by +I effect on α -carbon which in turn exerts the same effect on COOH group and hinders release of H^+ .

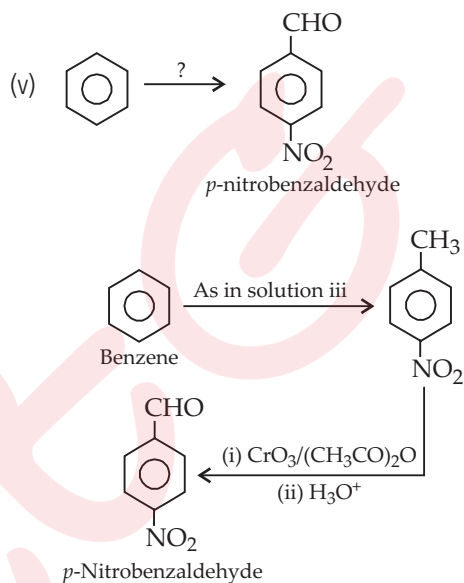
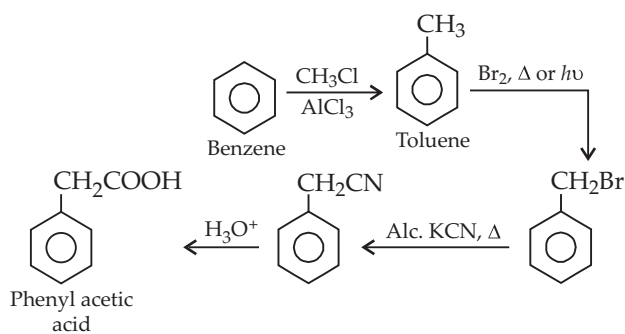
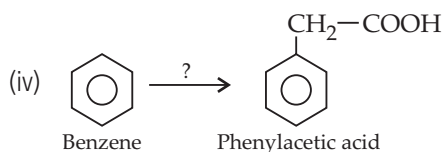
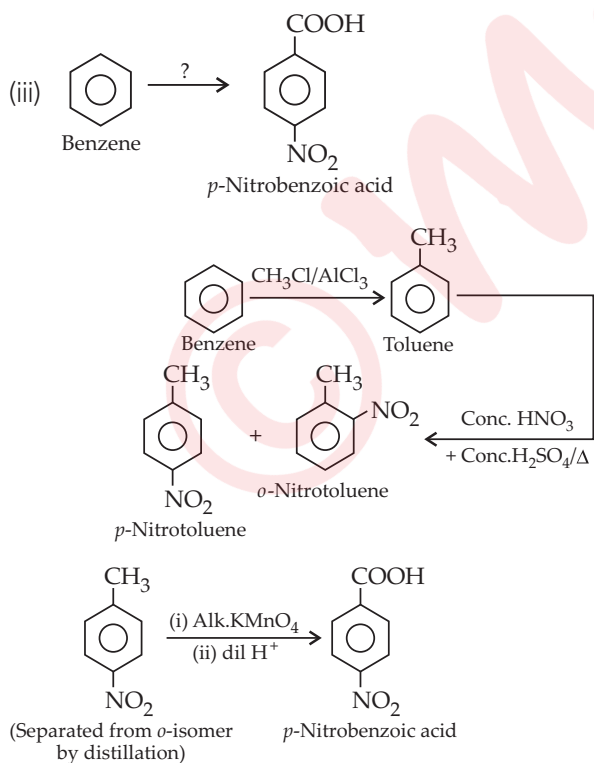
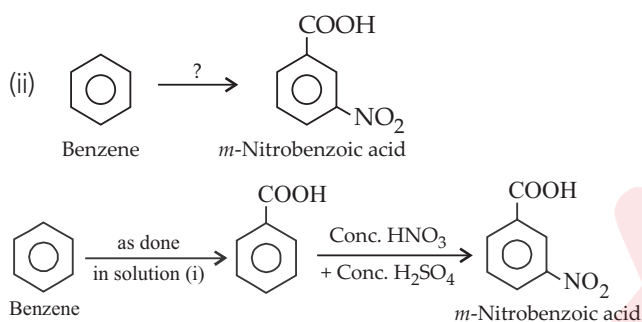
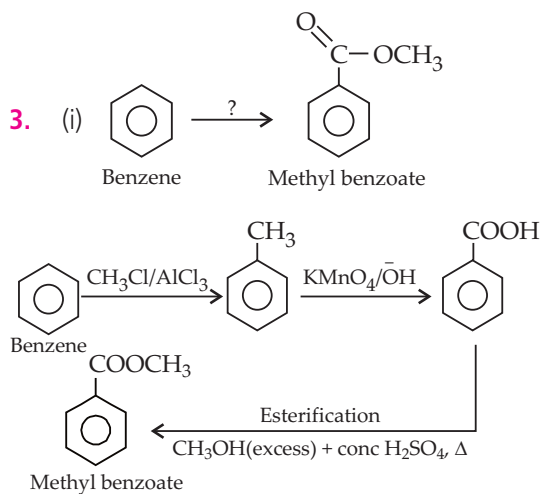
(iii) In benzoic acid, the attachment of electron withdrawing groups (EWG) on the benzene ring makes the $\text{O}-\text{H}$ bond of COOH group polar and H is lost as H^+ .

Therefore, the order is,

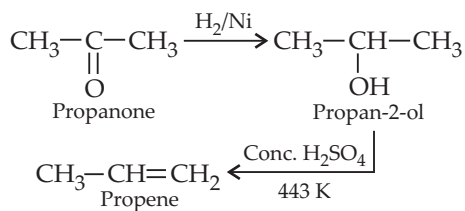


2. The given set of compounds may be distinguished by the following reaction.

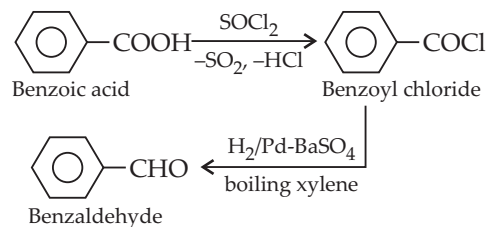
Compound Reagent ↓ →	Compound I	Compound II
(i) Ammoniacal silver nitrate $2[\text{Ag}(\text{NH}_3)_2]^+$ (Tollens' reagent)	$\text{CH}_3-\text{CH}_2-\text{CHO}$ Propanal \downarrow $\text{CH}_3\text{CH}_2\text{COO}^- + 2\text{Ag} + 2\text{H}_2\text{O} + 4\text{NH}_3$ Silver mirror	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \end{array}$ Propanone \rightarrow No reaction
(ii) NaOI	$\begin{array}{c} \text{O}=\text{C}-\text{CH}_3 \\ \\ \text{C}_6\text{H}_5 \end{array} \xrightarrow{\text{Iodoform test}} \begin{array}{c} \text{COO}^-\text{Na}^+ \\ \\ \text{C}_6\text{H}_5 \end{array} + \text{CHI}_3 \downarrow$ Acetophenone Yellow ppt.	$\begin{array}{c} \text{O} \\ \\ \text{C}_6\text{H}_5-\text{C}-\text{C}_6\text{H}_5 \end{array} \rightarrow$ No reaction Benzophenone
(iii) NaHCO_3	$\begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_5 \end{array} \rightarrow$ No reaction Phenol	$\begin{array}{c} \text{COOH} \\ \\ \text{C}_6\text{H}_5 \end{array} \rightarrow \begin{array}{c} \text{COO}^-\text{Na}^+ \\ \\ \text{C}_6\text{H}_5 \end{array} + \text{H}_2\text{O} + \text{CO}_2 \uparrow$ Benzoic acid Effervescence
(iv) NaHCO_3	$\begin{array}{c} \text{COOH} \\ \\ \text{C}_6\text{H}_5 \end{array} \rightarrow \begin{array}{c} \text{COO}^-\text{Na}^+ \\ \\ \text{C}_6\text{H}_5 \end{array} + \text{H}_2\text{O} + \text{CO}_2 \uparrow$ Benzoic acid Effervescence	$\begin{array}{c} \text{COOC}_2\text{H}_5 \\ \\ \text{C}_6\text{H}_5 \end{array} \rightarrow$ No reaction Ethyl benzoate
(v) NaOI	$\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\underset{ }{\text{C}}}-\text{CH}_2-\text{CH}_3 \rightarrow$ Pentan-3-one No reaction	$\text{CH}_3-\overset{\text{O}}{\underset{ }{\text{C}}}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \rightarrow$ Pentan-2-one $\text{CHI}_3 \downarrow + \text{CH}_3(\text{CH}_2)_2-\overset{\text{O}}{\underset{ }{\text{C}}}-\text{O}^-$ Iodoform (yellow ppt.)
(vi) NaOI	$\begin{array}{c} \text{CHO} \\ \\ \text{C}_6\text{H}_5 \end{array} \rightarrow$ No reaction Benzaldehyde	$\begin{array}{c} \text{O}=\text{C}-\text{CH}_3 \\ \\ \text{C}_6\text{H}_5 \end{array} \rightarrow \begin{array}{c} \text{COO}^-\text{Na}^+ \\ \\ \text{C}_6\text{H}_5 \end{array} + \text{CHI}_3 \downarrow$ Acetophenone Yellow ppt.
(vii) NaOI	$\text{CH}_3\text{CHO} \rightarrow 2\text{CHI}_3 \downarrow + \text{HCOO}^-\text{Na}^+$ Ethanal Yellow ppt.	$\text{CH}_3\text{CH}_2\text{CHO} \rightarrow$ No reaction Propanal



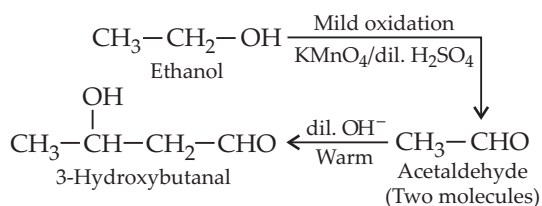
4. (i) Propanone to Propene :

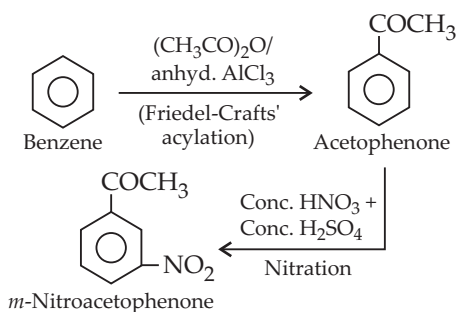


(ii) Benzoic acid to Benzaldehyde :

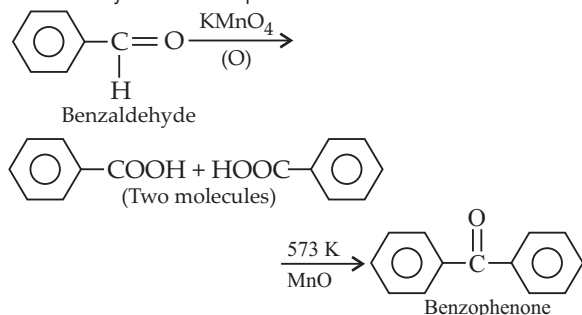


(iii) Ethanol to 3-Hydroxybutanal :

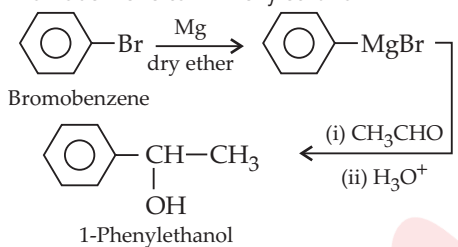


(iv) Benzene to *m*-Nitroacetophenone :

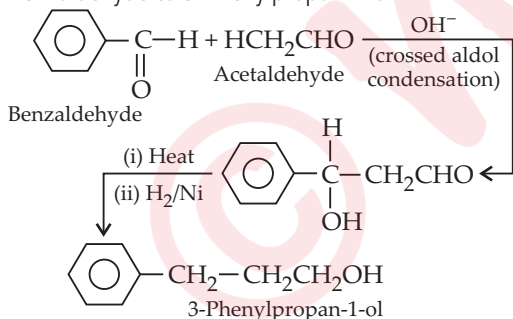
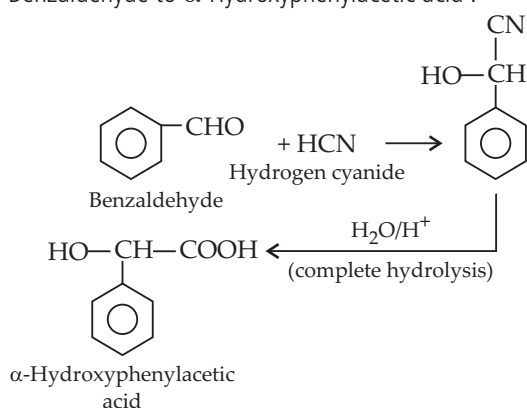
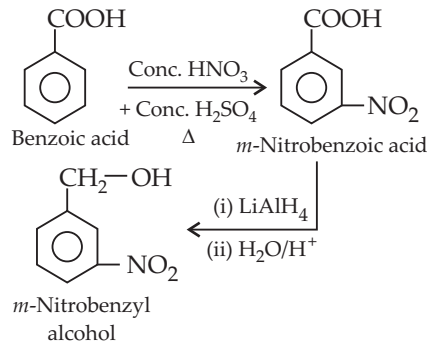
(v) Benzaldehyde to Benzophenone :



(vi) Bromobenzene to 1-Phenylethanol

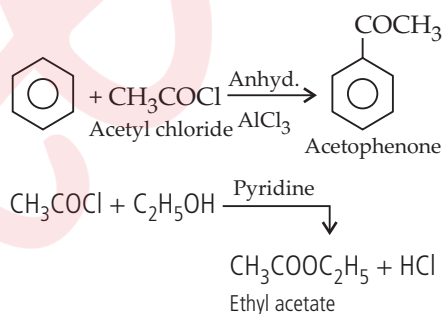


(vii) Benzaldehyde to 3-Phenylpropan-1-ol :

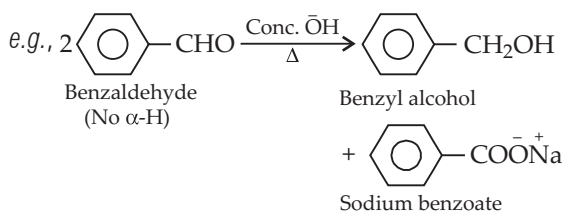
(viii) Benzaldehyde to α -Hydroxyphenylacetic acid :(ix) Benzoic acid to *m*-Nitrobenzyl alcohol :**5. (i) Acetylation :** Acetylation is the process of

introducing $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ group in compounds that contain a replaceable hydrogen atom. The best example of acetylation is Friedel-Crafts acylation reaction where RCO group is introduced on the benzene ring.

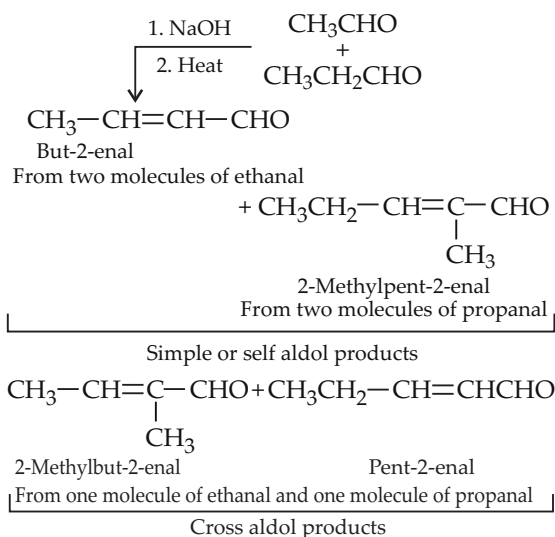
Reagents employed for the purpose of acylation are acyl chloride, acid anhydride etc. *e.g.*, Friedel-Crafts acylation:



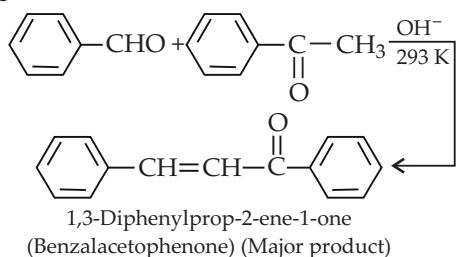
(ii) Cannizzaro reaction : Cannizzaro reaction is given by aldehydes or ketones that lack, α -hydrogen atom. Such carbonyl compounds in the presence of conc. NaOH and heat undergo disproportionation reaction to produce the corresponding carboxylate ion and alcohol.



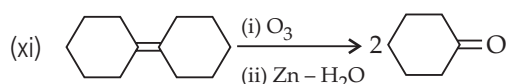
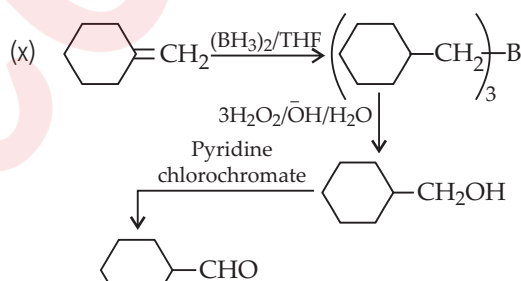
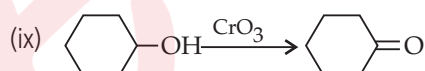
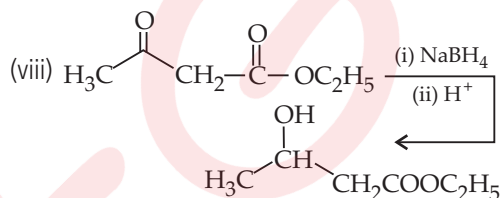
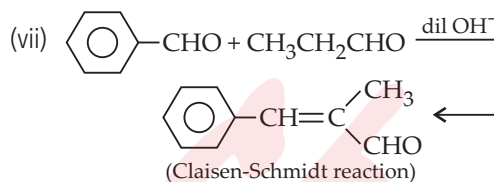
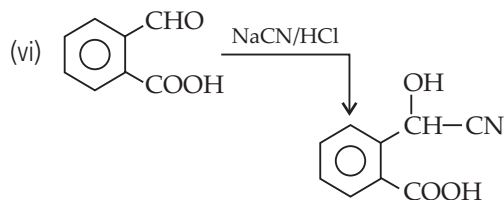
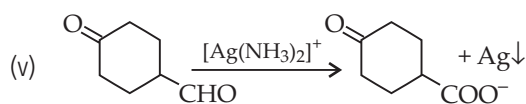
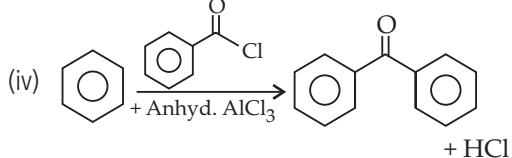
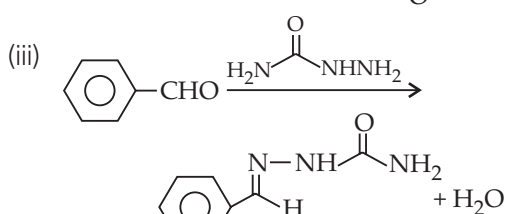
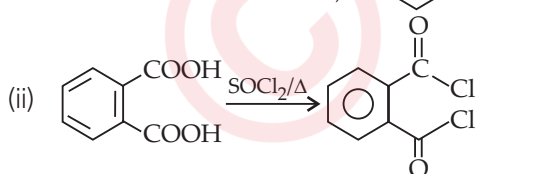
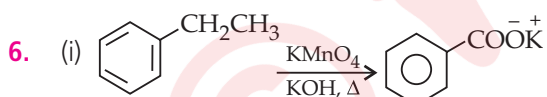
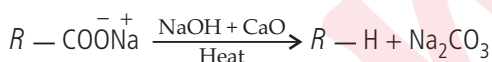
(iii) Cross-aldol condensation : Aldol condensation is the reaction that takes place, when aldehydes or ketones with at least one α -H atom react in the presence of dilute alkali to produce β -hydroxy aldehydes or ketones. When two different aldehydes or ketones are taken, it gives a mixture of products. Such a reaction is called cross-aldol condensation.



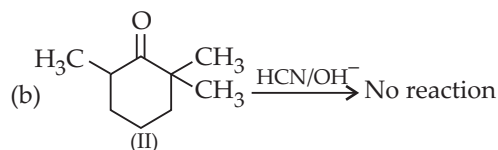
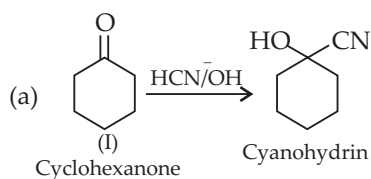
Ketones can also be used as one component in the cross aldol reactions



(iv) Decarboxylation : Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3 : 1). The reaction is called decarboxylation.



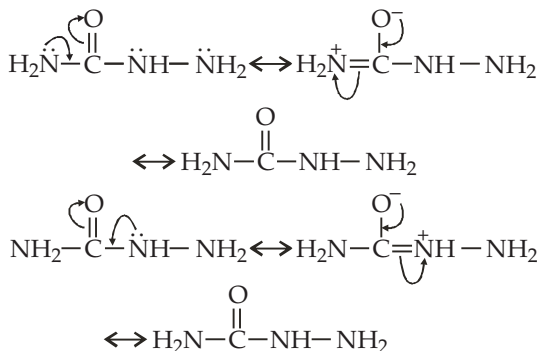
7. (i) Consider the following reactions :



Reaction (a) is an example of cyanohydrin formation by the nucleophilic attack of cyanide ion on the carbonyl carbon. In cyclohexanone, this attack takes place easily and cyanohydrin is formed. But in II, attack of the Nu⁻ is sterically hindered due

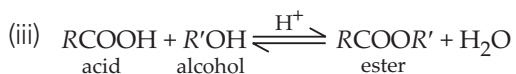
to the presence of the three methyl groups. As a result, the reaction does not occur.

(ii) Semicarbazide has the following resonance structures arising due to the electron withdrawing nature of the O atom.



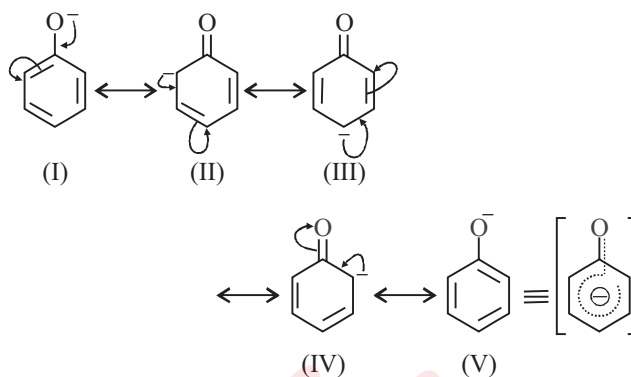
From the given structures we find that the lone pair of electrons on N atoms on either side of >C=O group are delocalised, involved in resonance. Therefore, they are not available for carrying out the nucleophilic attack on the aldehyde or ketone. But, the $-\text{NH}_2$ (terminal one) is intact, *i.e.* it is not involved in resonance and thus its lone pair is available for attack on carbonyl compound.

This is why the semicarbazone is formed through this N atom only.

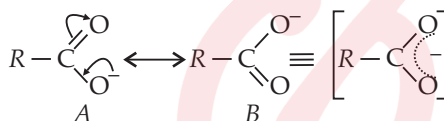


The esterification reaction is a reversible reaction. If water and the ester are allowed to remain in the reaction mixture the hydrolysis of the ester would take place. Hence, water or ester should be removed as soon as it is formed.

8. (i) Phenoxide ion has the following resonating structures :



Carboxylate ion has the following resonance structures.



(ii) Phenoxide ion is a resonance hybrid of structures I to V, where each structure has a contribution of 20% in the resonance hybrid. On the other hand, each of the two contributing structures of carboxylate ion contribute 50% towards the resonance hybrid. Therefore, the carboxylate ion tends to be more stable than the phenoxide ion and hence has higher acidity.

(iii) The negative charge that rests on the electronegative O atom in carboxylate ion. We know that the presence of negative charge on an electronegative atom makes the ion more stable. For the same reason RCOO^- is more stable than the phenoxide ion where the oxygen has no negative charge on it. For the above two reasons carboxylate ion is more stable and has higher acidity than phenol.

