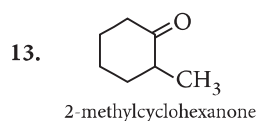
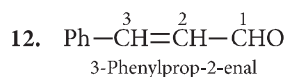
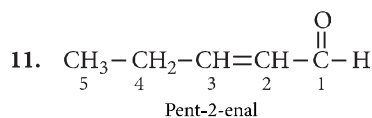
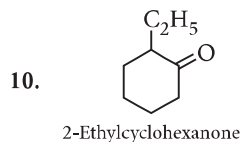
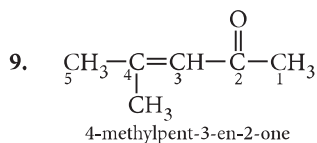
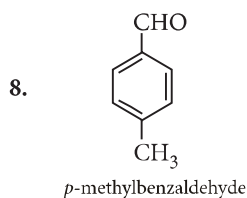
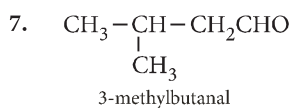
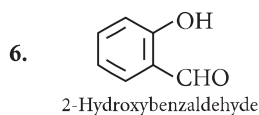
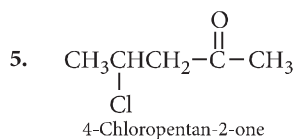
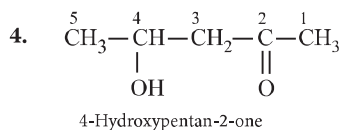
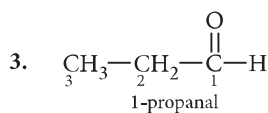
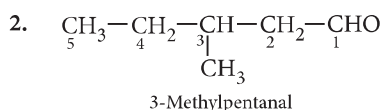
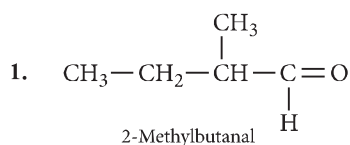
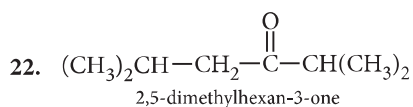
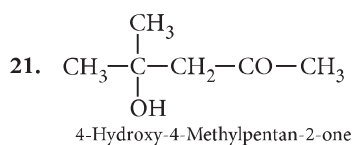
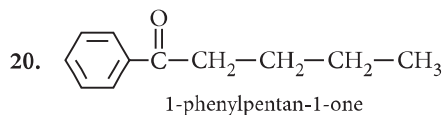
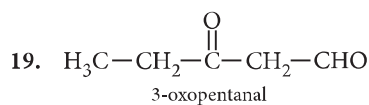
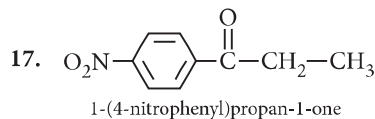
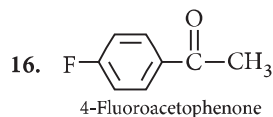
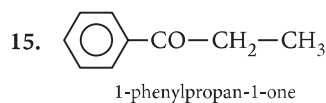
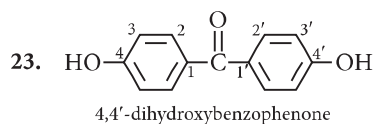


Detailed Solutions

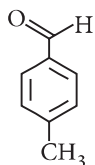


14. Refer to answer 9.

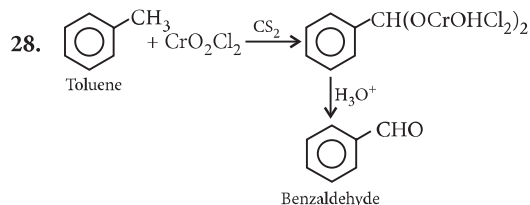
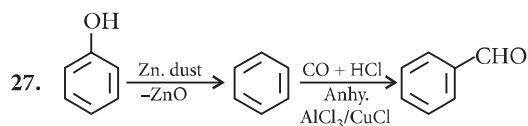
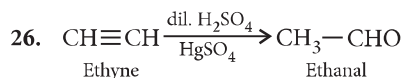
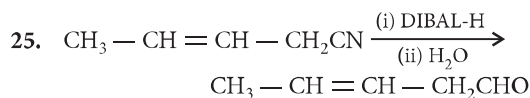
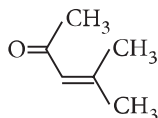




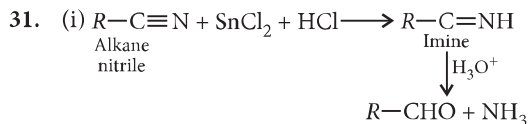
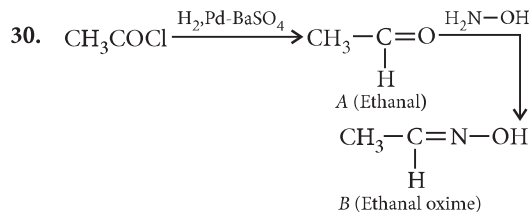
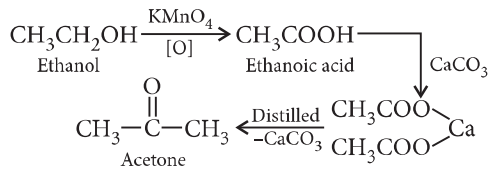
24. (i) *p*-Methylbenzaldehyde :



(ii) 4-Methylpent-3-en-2-one :



29. Ethanol to acetone :



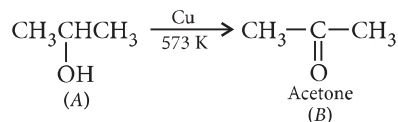
(ii) Refer to answer 28.

32. Compound B gives positive iodoform test, it means it contains  $-\text{COCH}_3$  (methyl ketone) group i.e., it is a ketone. Moreover, B is obtained by the oxidation of A, thus A must be a 2° alcohol. (As only 2° alcohol give ketones on oxidation with Cu at 573 K. Hence, the structure of compound A is  $\text{RCH}(\text{OH})\text{CH}_3$ )

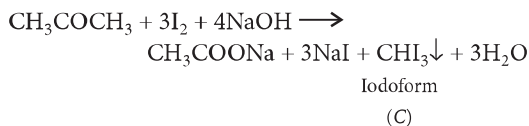
Comparing with the given molecular formula gives  $\text{R} = \text{CH}_3$ .

Thus, compound A is  $\text{CH}_3\underset{\text{OH}}{\text{CH}}\text{CH}_3$   
(Propan-2-ol)

The reaction are as follows :



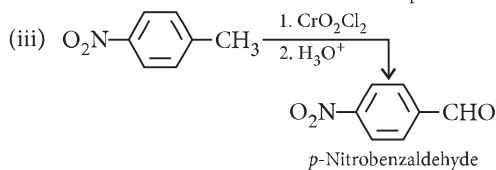
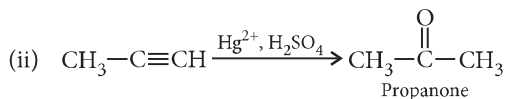
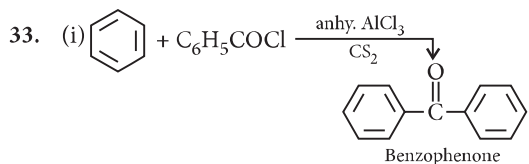
Acetone  $\xrightarrow[\text{solution}]{\text{Fehling}}$  No reaction



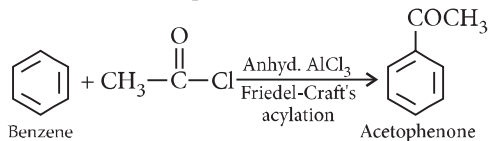
Thus, A =  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$

B =  $\text{CH}_3\text{COCH}_3$

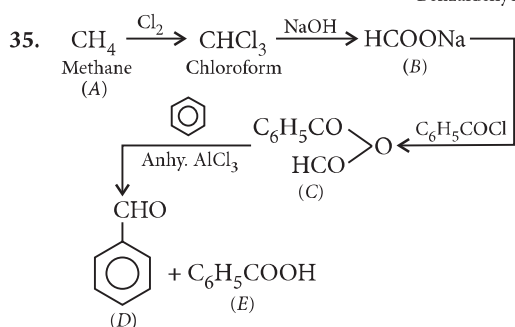
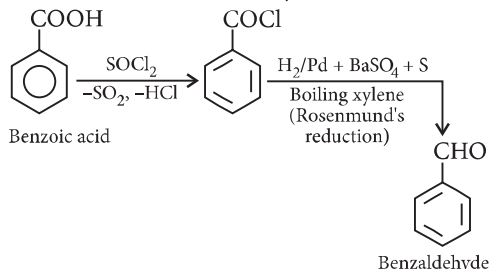
C =  $\text{CHI}_3$



34. (i) Refer to answer 29.  
 (ii) Benzene to acetophenone.



- (iii) Benzoic acid to benzaldehyde.



36. The boiling points of aldehydes and ketones are lower than that of corresponding alcohols and acids due to absence of intermolecular H-bonding in aldehydes and ketones.

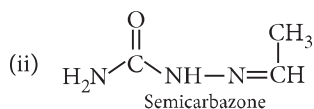
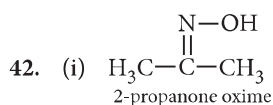
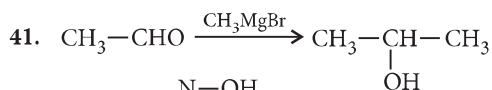
37. Refer to answer 36.

38. Benzaldehyde and acetophenone can be distinguished by Tollens' test.

Benzaldehyde will form silver mirror, on treatment with Tollens' reagent whereas acetophenone will not show Tollens' Test.

39. (i) Lithium aluminium hydride ( $\text{LiAlH}_4$ ).

40. Propanal and propanone can be distinguished by their reactions with Tollens' reagent. Propanal will form the silver mirror, but propanone does not react.



43. Refer to answer 38.

44. (i) Benzaldehyde and benzoic acid can be distinguished by sodium bicarbonate test.

Benzoic acid will give effervescence with  $\text{NaHCO}_3$  but benzaldehyde will not react.

(ii) Propanal and propanone can be distinguished by their reactions with Tollens' reagent.

Propanal will form the silver mirror, but propanone does not react.

45. It is a nucleophilic addition reaction, in which  $\text{CN}^-$  acts as a nucleophile.  $\text{CH}_3\text{CHO}$  undergoes nucleophilic addition reactions faster than  $\text{CH}_3\text{COCH}_3$  as in  $\text{CH}_3\text{COCH}_3$  there are two electron releasing methyl groups attached to the carbonyl carbon that hinders the approach of nucleophile to carbonyl carbon and reduce the electrophilicity of the carbonyl group while in  $\text{CH}_3\text{CHO}$ , there is only one methyl group attached to carbonyl carbon.

46. Refer to answer 45(ii).

47. Propanal and Butan-2-one can be distinguished by their reactions with tollens' reagent. Propanal will form the silver mirror, but Butan-2-one does not react.

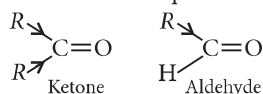
48. Ethanal and propanal can be distinguished by iodoform test.

Yellow precipitate of iodoform will be formed from ethanal on heating with iodine and sodium hydroxide solution.

49. In strongly acidic medium ammonia derivatives being basic will react with acids and will not react with carbonyl compound. In basic medium,  $\text{OH}^-$  will attack carbonyl group.

Therefore, pH of a reaction should be carefully controlled.

50. Ketones are less reactive than aldehydes towards nucleophilic addition reactions because :  
 The two electron releasing alkyl groups decrease the magnitude of positive charge on carbonyl carbon and make it less susceptible to nucleophilic attack.

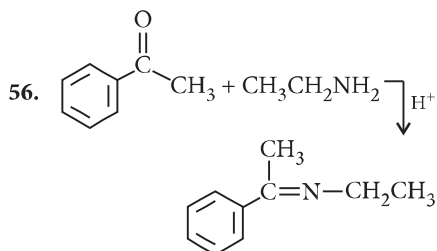
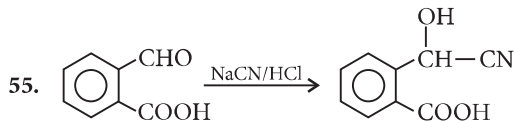
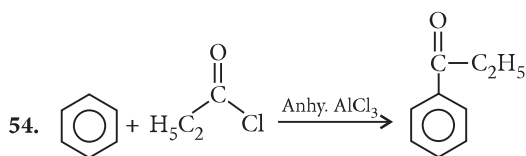
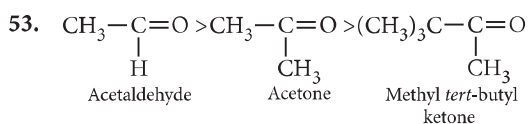


The two bulkier alkyl groups hinder the approach of the nucleophile to the carbonyl carbon. This is called steric factor.

51. Butanone < propanone < propanal < ethanal.

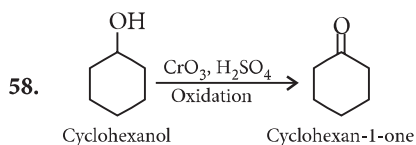
52. Acetophenone and benzophenone can be distinguished by iodoform test.

Acetophenone will give the yellow precipitate of iodoform, but benzophenone will not react.

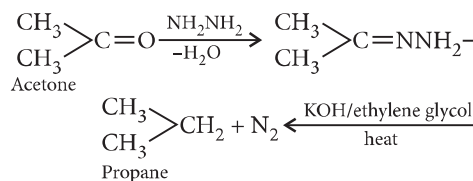


57. Tollens' reagent is an ammoniacal silver nitrate solution.

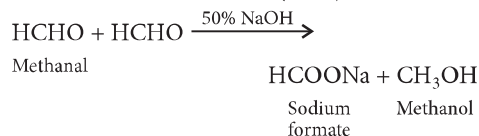
Tollens' reagent is used to test an aldehyde. Both aliphatic and aromatic aldehydes reduce Tollens' reagent and give silver mirror.



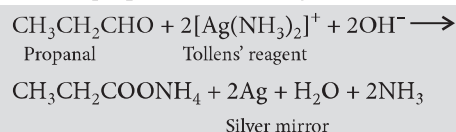
59. **Wolff-Kishner reduction reaction** : The carbonyl group of aldehydes and ketones is reduced to  $\text{CH}_2$  group on treatment with hydrazine followed by heating with potassium hydroxide in a high boiling solvent such as ethylene glycol.



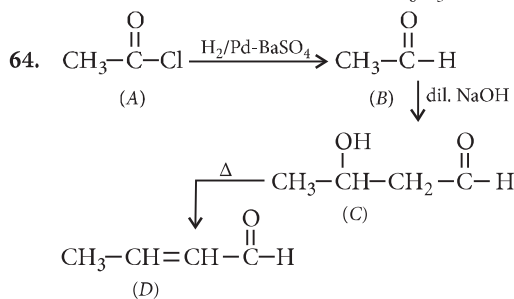
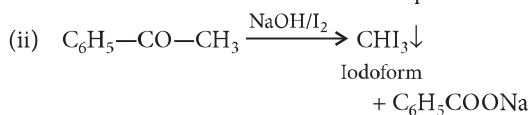
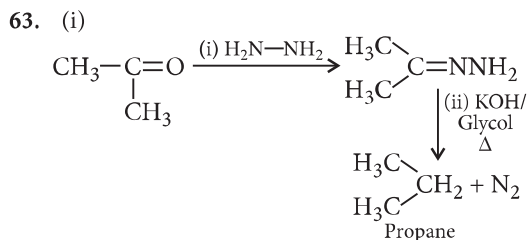
60. **Cannizzaro's reaction** : Aldehydes which do not contain  $\alpha$ -H atom undergo disproportionation when heated with concentrated (50 %) NaOH.



61. Propanal reduces Tollens' reagent into silver mirror while propanone does not give this test.

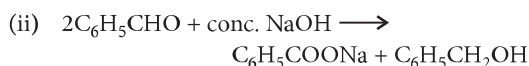
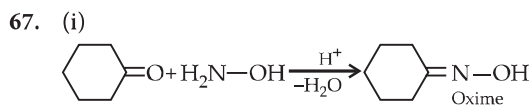
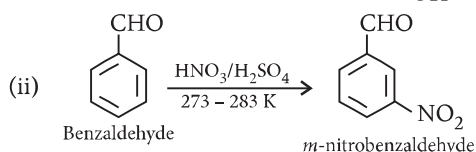
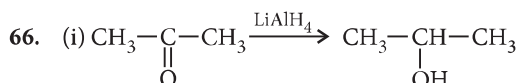
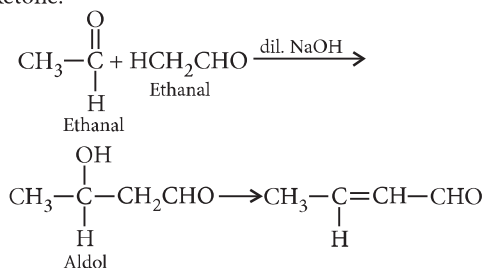


62. Refer to answer 60.



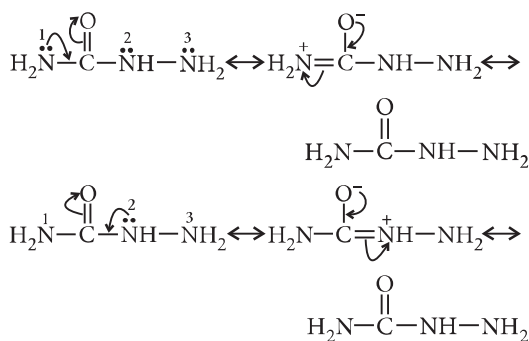
65. (i) **Acetylation** : Introduction of acetyl group  $\left( -\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3 \right)$  in alcohols, phenols or amines is called their acetylation.

(ii) **Aldol condensation** : Two molecules of an aldehyde or ketones having at least one  $\alpha$ -hydrogen atom condense in the presence of a dilute alkali to give  $\beta$ -hydroxyaldehyde or  $\beta$ -hydroxyketone which upon heating give  $\alpha,\beta$ -unsaturated aldehyde or ketone.



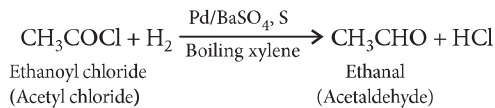
68. (i) Refer to answer 45.

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

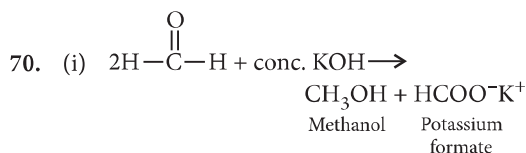


Lone pairs of N-1 and N-2 are involved in conjugation with  $\text{>C}=\text{O}$  group while that of N-3 is not involved in resonance thus, it is involved in the formation of semicarbazone.

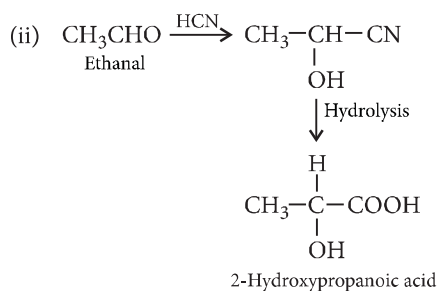
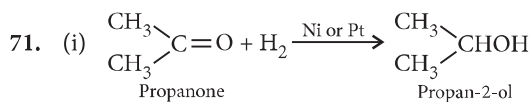
69. (i) **Rosenmund's reaction** :



(ii) Refer to answer 60.

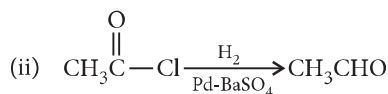
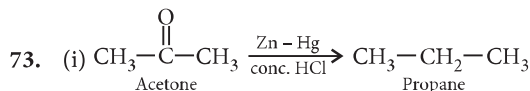


(ii) Refer to answer 66(ii).



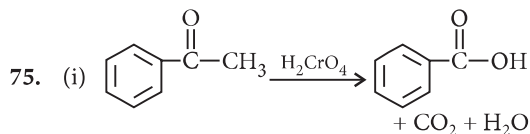
72.

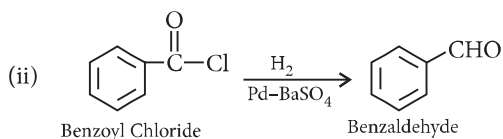
(a) NaOI	$\text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ Pentan-3-one $\longrightarrow$ No reaction	$\text{CH}_3-\text{C}(=\text{O})-(\text{CH}_2)_2\text{CH}_3$ Pentan-2-one gives iodoform test.
(b) NaOI	$\text{CH}_3\text{CHO}$ Ethanal gives iodoform test.	$\text{CH}_3\text{CH}_2\text{CHO} \longrightarrow$ Propanal No reaction



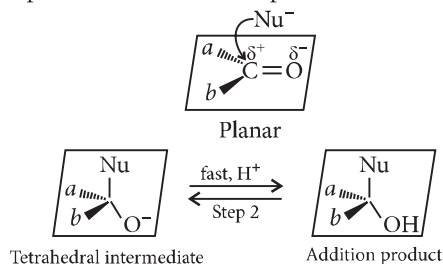
74. (i) Refer to answer 46.

(ii) Refer to answer 38.



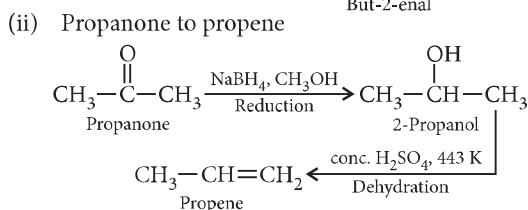
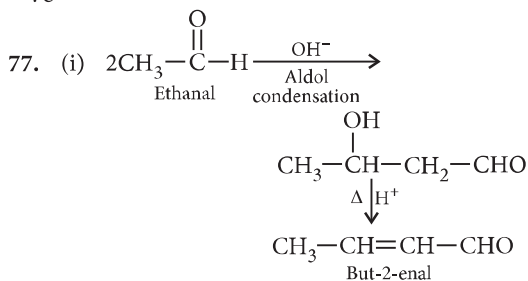


**76. Mechanism of nucleophilic addition reactions :**  
Nucleophile attacks from the top face :

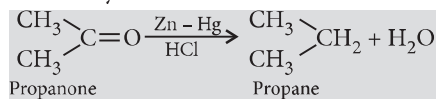


A nucleophile attacks the electrophilic carbon atom from a direction perpendicular to the plane of  $sp^2$  hybridised orbital of carbonyl carbon. The hybridisation of carbon changes from  $sp^2$  to  $sp^3$  in this process and a tetrahedral alkoxide intermediate is produced.

This intermediate captures a proton from the reaction medium to give the electrically neutral product. The net result is addition of  $\text{Nu}^-$  and  $\text{H}^+$  across the carbon oxygen double bond.



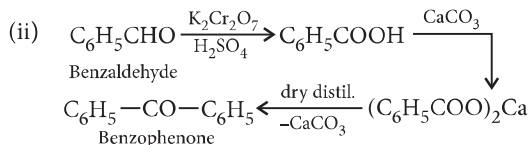
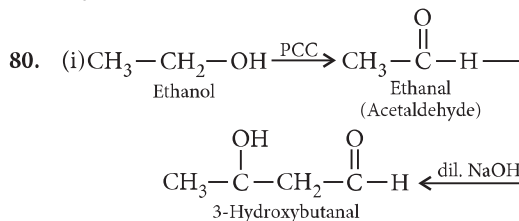
**78. (i) Clemmensen reduction :** The carbonyl group of aldehydes and ketones is reduced to  $\text{CH}_2$  group on treatment with zinc amalgam and concentrated hydrochloric acid.



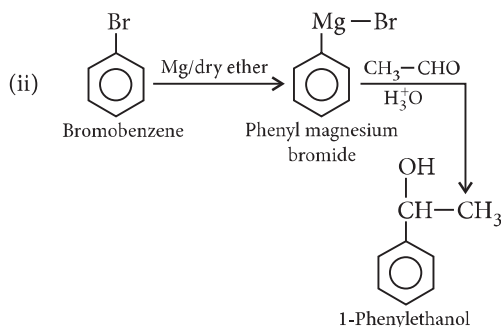
(ii) Refer to answer 60.

79. (i) Refer to answer 75(ii).

(ii) Refer to answer 33(i).



81. (i) Refer to answer 77(ii).

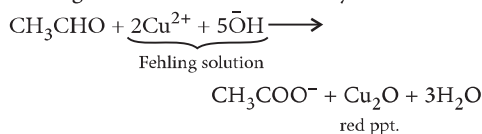


82. (i) Refer to answer 50.

(ii) Aldehydes and ketones undergo a number of addition reactions as both possess the carbonyl functional group which reacts with a number of nucleophiles such as HCN,  $\text{NaHSO}_3$ , alcohols, ammonia derivatives and Grignard reagents.

**83. (i) Distinction between acetaldehyde and benzaldehyde :** Acetaldehyde and benzaldehyde can be distinguished by Fehling solution.

Acetaldehyde gives red coloured precipitate with Fehling solution while benzaldehyde does not.



(ii) Refer to answer 46.

84. (i) Refer to answer 60.

(ii) Refer to answer 65(i).

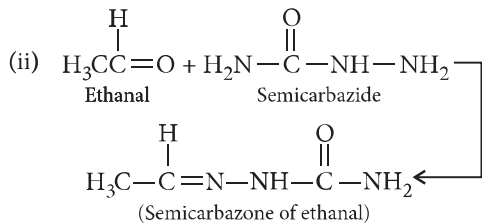
85. (i) Refer to answer 52.

(ii) Refer to answer 48.

86. (i) Refer to answer 69(i).

(ii) Refer to answer 60.

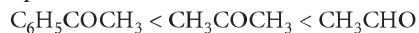
87. (i) Refer to answer 60.



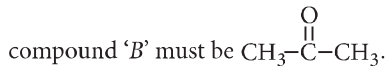
(iii) Refer to answer 44(ii).

88. (i) Refer to answer 59.

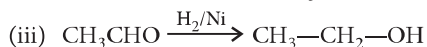
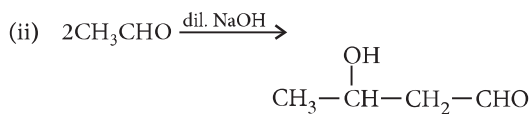
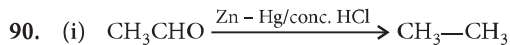
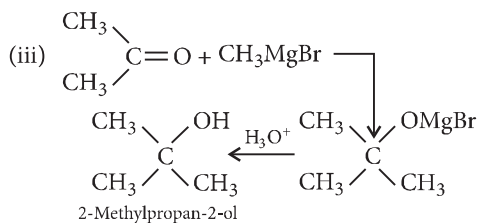
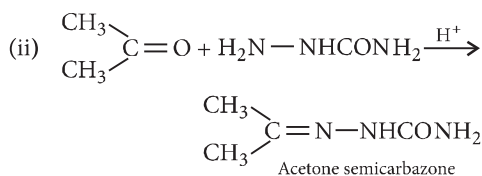
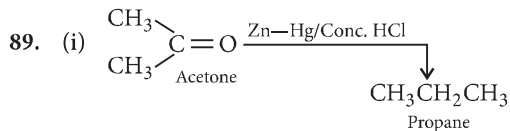
(ii) Increasing order of reactivity towards nucleophilic addition reaction :



(iii) Formula of compounds A and B = C<sub>3</sub>H<sub>6</sub>O  
B forms yellow precipitate of iodoform. Hence, B must contain —COCH<sub>3</sub> group. Therefore,



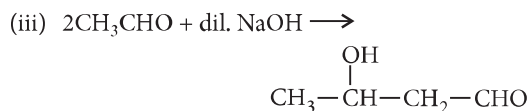
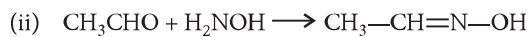
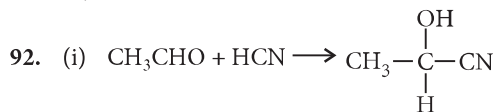
A does not give iodoform test and it is functional isomer of B thus, it may be CH<sub>3</sub>CH<sub>2</sub>CHO.



91. (i) Refer to answer 59.

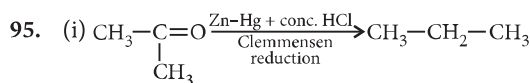
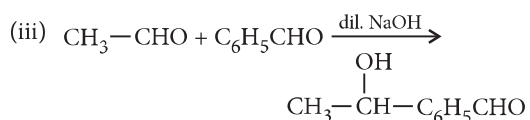
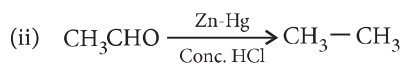
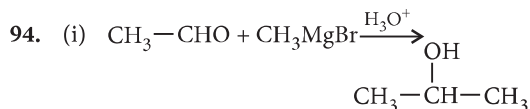
(ii) Refer to answer 65(ii).

(iii) Refer to answer 60.

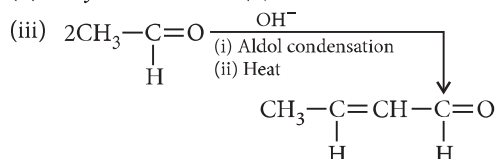


93. (a) Refer to answers 69(i) and 60.

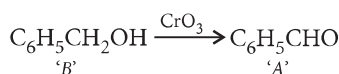
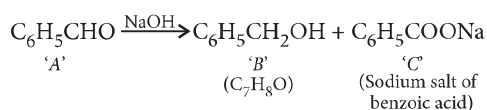
(b) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>—CO—CH<sub>3</sub> will give iodoform test because it contains acetyl group.

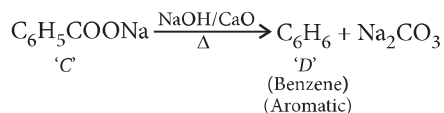


(ii) Refer to answer 75(ii).

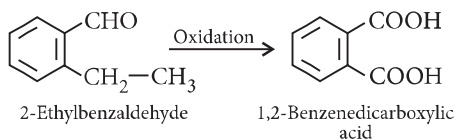


96. Benzaldehyde has a characteristic odour. Reaction of 'A' with NaOH appears to be Cannizzaro reaction which gives 'B' (benzyl alcohol) and 'C' (Sodium salt of benzoic acid). Oxidation of alcohols gives aldehydes. Sodium salt of benzoic acid on heating with soda lime given benzene (D).

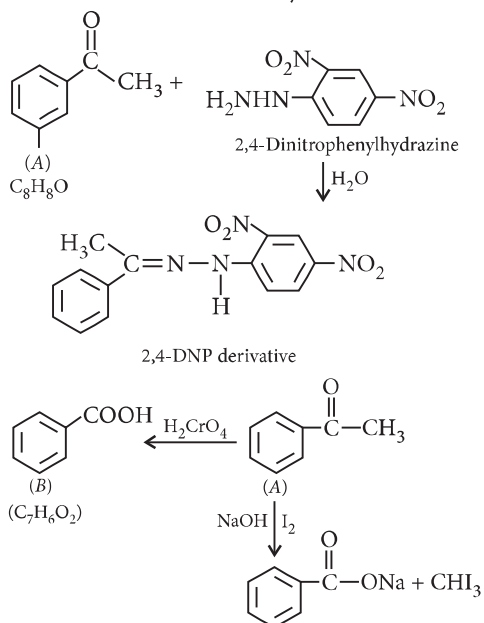




97. The compound forms 2,4-DNP derivative. It shows that it is a carbonyl compound. Further it reduces Tollens' reagent which shows that it contains aldehydic group. It undergoes Cannizzaro reaction indicating that aldehyde group is without any  $\alpha$ -hydrogen. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid which shows that there are two carbon residues on benzene ring. Since the molecular formula is  $\text{C}_9\text{H}_{10}\text{O}$ , it fits into the structure, 2-ethylbenzaldehyde.



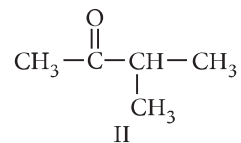
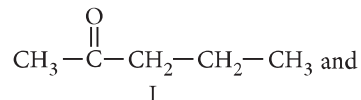
98. (A) forms, 2, 4-DNP derivative. Therefore, it is an aldehyde or a ketone. Since it does not reduce Tollens' or Fehling reagent, (A) must be a ketone. (A) responds to iodoform test. Compound (B), being an oxidation product of a ketone should be a carboxylic acid. The molecular formula of (B) indicates that it should be benzoic acid and compound (A) should, therefore, be a mono-substituted aromatic methyl ketone.



99. The given compound does not reduce Tollens' reagent, so it is not an aldehyde but the formation of addition compound with sodium hydrogen sulphite indicates it to be a carbonyl compound. Since this compound gives positive iodoform test, so it should

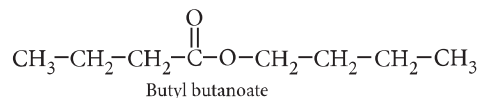
contain  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$  group.

On the basis of this information, two possible structures are written as under :

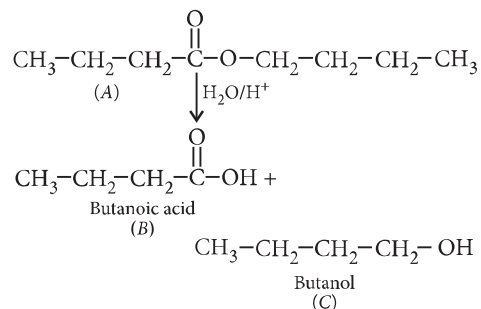


On oxidation, this compound gives ethanoic and propanoic acids which confirm its structure to be I.

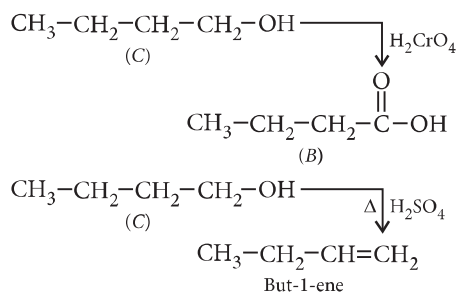
100. Compound 'A' ( $\text{C}_8\text{H}_{16}\text{O}_2$ ) on hydrolysis gives an acid 'B' and an alcohol 'C'. It shows that 'A' is an ester. Since the oxidation of alcohol 'C' also gives the acid 'B' indicates that 'B' and 'C' both contain same number of carbon atoms, *i.e.* four carbon atoms each and same arrangement of atoms. Formation of but-1-ene on dehydration of 'C' indicates it to be butan-1-ol, so the possible structure for 'A' could be



The various reactions involved are written as follows :







101. Calculation of the empirical formula of the compound :

Element	Percentage	Atomic mass	Relative numbers of atoms	Simple molar ratio
C	69.77	12	$\frac{69.77}{12} = 5.814$	5
H	11.63	1	$\frac{11.63}{1} = 11.63$	10
O	18.6	16	$\frac{18.6}{16} = 1.163$	1

So, the empirical formula is  $\text{C}_5\text{H}_{10}\text{O}$

Empirical formula mass

$$= (5 \times 12) + (10 \times 1) + (1 \times 16) = 86$$

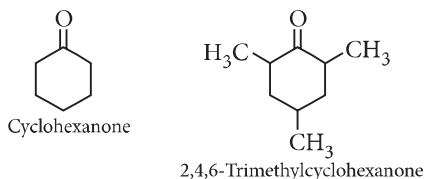
Given that molecular mass of the compound = 86

Hence, the molecular formula of the compound is  $\text{C}_5\text{H}_{10}\text{O}$

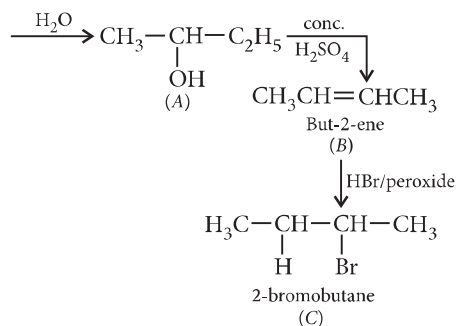
Refer to answer 99.

102. (a) (i) Refer to answer 68(ii).

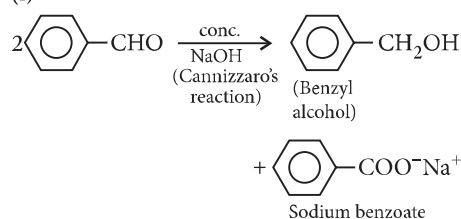
(ii) Formation of cyanohydrin involves the nucleophilic attack of cyanide ions ( $\text{CN}^-$ ) at the carbonyl carbon. In cyclohexanone, reaction proceeds but in 2,4,6-trimethylcyclohexanone, the methyl groups cause steric hindrance and yields are poor.



(b) Refer to answer 97.

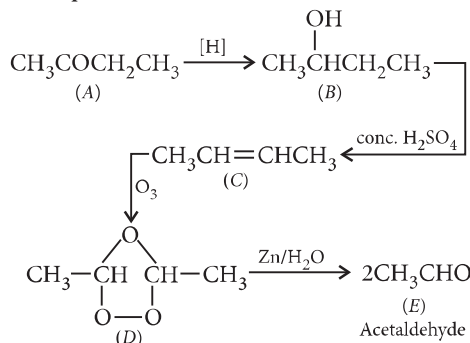


(b) (i)

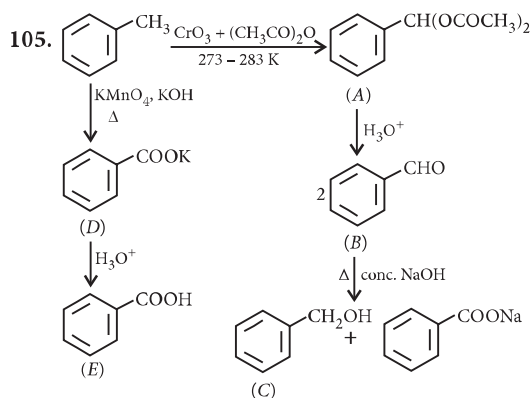
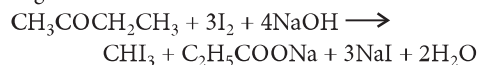


(ii) Refer to answer 70(ii).

104. The equations involved are :



A gives haloform reaction as :

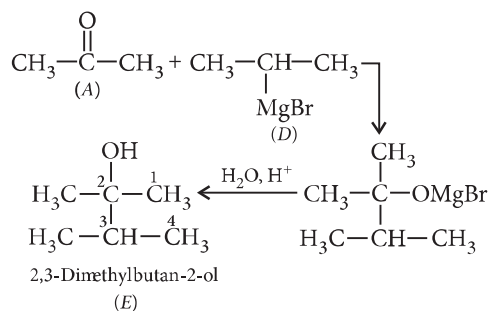
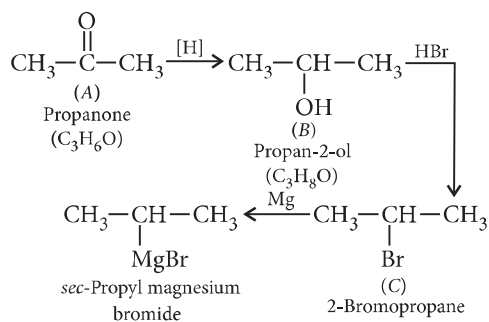


106. (a) (i) Refer to answer 60.

(ii) Refer to answer 78(i).

(b) Refer to answer 101.

107. Ketones are oxidised under vigorous conditions.



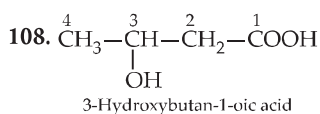
Therefore, (A) : Propanone

(B) : Propan-2-ol

(C) : 2-Bromopropane

(D) : sec-Propyl magnesium bromide

(E) : 2,3-Dimethylbutan-2-ol

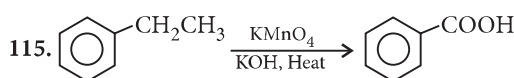
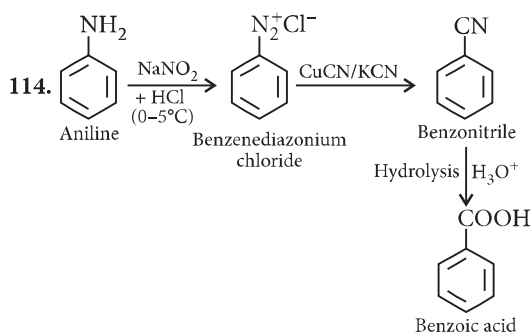
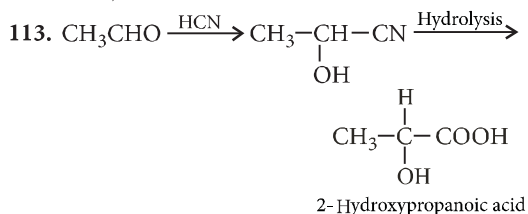


109. Hex-2-en-4-ynoic acid

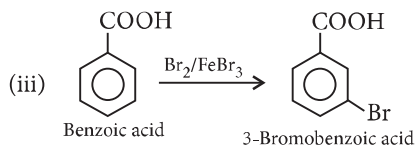
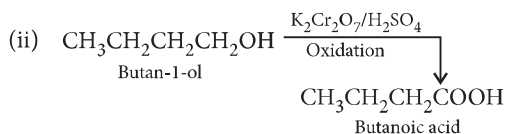
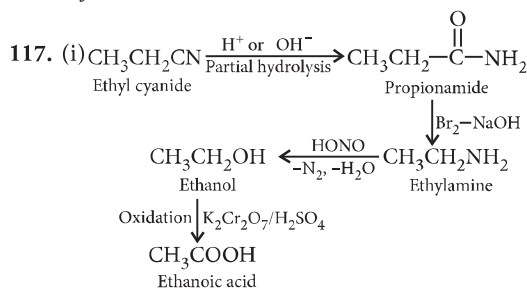
110. 3-Bromo-5-chloro Benzoic acid

111. Ethyl-4-chlorobenzoate

112. Alkaline potassium permanganate ( $\text{KMnO}_4$ ,  $\text{KOH}$ )

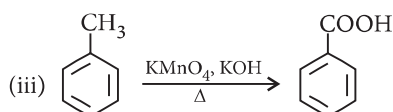


116. Refer to answer 115.

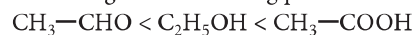


118. (i) Refer to answer 117(i).

(ii) Refer to answer 117(ii).

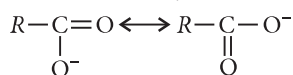


119. Increasing order of boiling point :

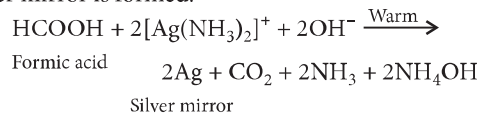


121. The carbonyl group in  $-\text{COOH}$  is inert and does not show nucleophilic addition reaction

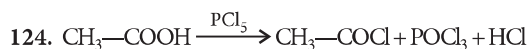
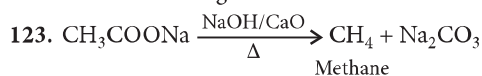
like carbonyl compound. It is due to resonance stabilisation of carboxylate ion :



122. Add Tollens' reagent to formic acid and warm. Silver mirror is formed.

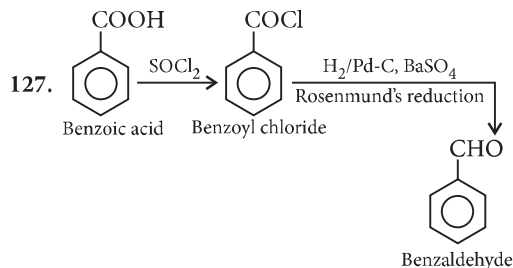
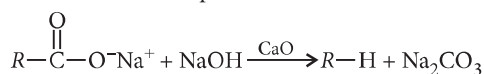


Acetic acid does not give this test.

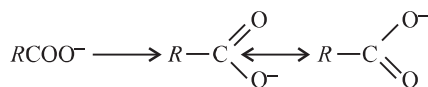
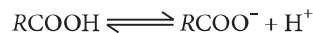


125. Refer to answer 124.

126. **Decarboxylation** : Sodium or potassium salt of carboxylic acids on heating with soda lime (NaOH and CaO), loses a molecule of carbon dioxide and alkanes are obtained as products.



128. In carboxylic acid C = O is in resonance and not available for reaction.

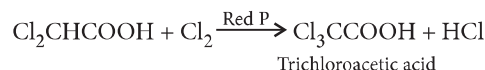
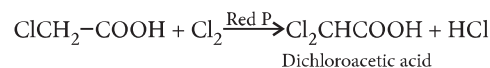
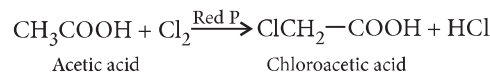


129. Phenol and benzoic acid can be distinguished by their reactions with sodium bicarbonate solution.

Benzoic acid will give effervescence with  $\text{NaHCO}_3$  but phenol will not react.

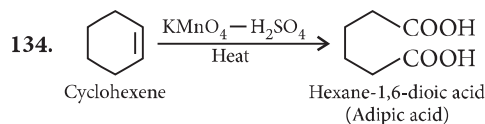
130. Benzoic acid and ethyl benzoate can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence with  $\text{NaHCO}_3$ .

131. **Hell-Volhard-Zelinsky reaction** : Carboxylic acids react with chlorine or bromine in the presence of phosphorous to give compounds in which  $\alpha$ -hydrogen atom is replaced by halogen atom.

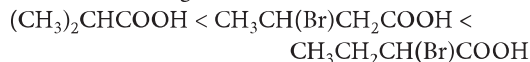


132. Refer to answer 117(iii).

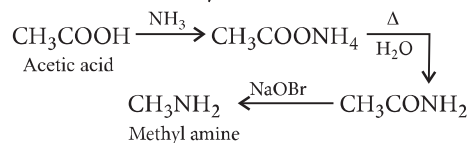
133. Chloroacetic acid has lower  $\text{p}K_a$  value than acetic acid; 'Cl' in chloroacetic acid shows  $-I$  effect, it creates less electron density on oxygen of carboxylic acid. Thus, release of proton becomes easier. In case of acetic acid, the state of affair is just opposite. Hence, chloroacetic acid is stronger than acetic acid.



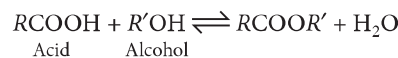
135. We know that  $+I$ -effect decreases while  $-I$ -effect increases the acid strength of carboxylic acids. The overall acid strength increases in the order.



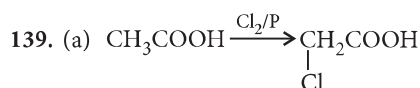
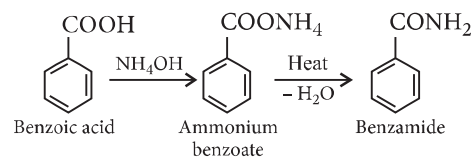
136. Acetic acid to methyl amine :



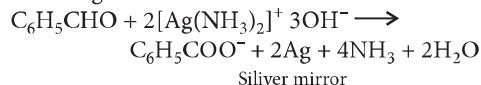
137. Fischer esterification :



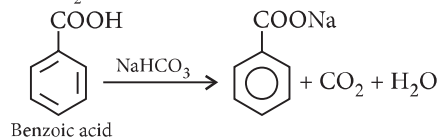
138. Benzoic acid to benzamide :



(b) Benzaldehyde when treated with ammoniacal silver nitrate gives silver mirror.

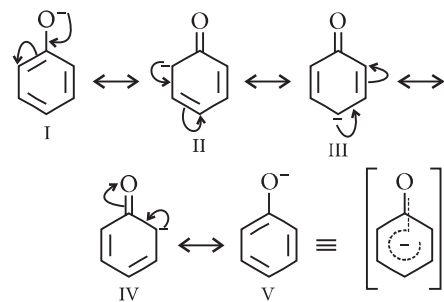


Benzoic acid reacts with sodium bicarbonate to liberate  $\text{CO}_2$ .

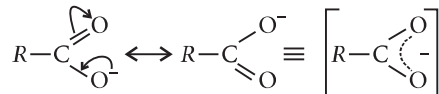


140. Refer to answer 133.

141. Phenoxide ion has the following resonating structures :



Carboxylate ion has the following resonating structures.

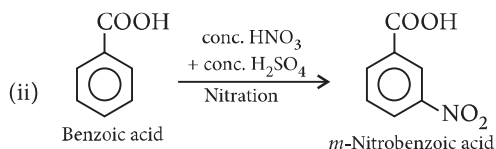
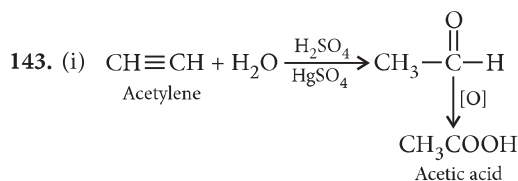


(i) Phenoxide ion is a resonance hybrid of structures I to V, where each structure has a contribution of 20% in the resonance hybrid. On the other hand, each of the two contributing structures of carboxylate ion contribute 50% towards the resonance hybrid. Therefore, the carboxylate ion tends to be more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

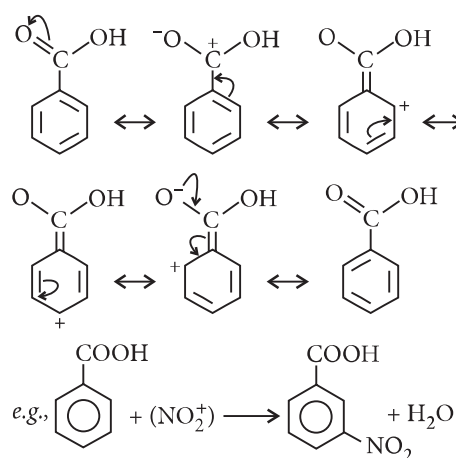
(ii) The negative charge rests on the electronegative O atom in carboxylate ion. The presence of negative charge on an electronegative atom makes the ion more stable. For the same reason  $\text{RCOO}^-$  is more stable than the phenoxide ion where the carbon has negative charge on it. For the above two reasons carboxylate ion is more stable and has higher acidity than phenol.

142. (i)  $\text{F}-\text{CH}_2\text{COOH} > \text{Cl}-\text{CH}_2\text{COOH}$ .

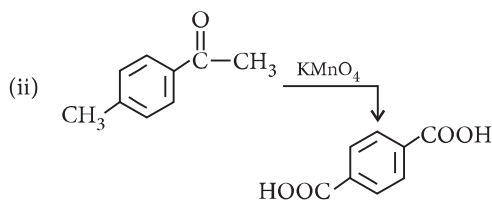
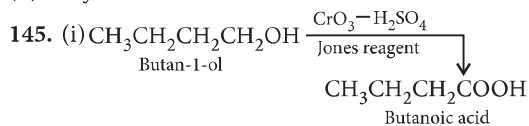
(ii)  $\text{CH}_3\text{COOH}$  is stronger than



144. (i) Electrophilic substitution in benzoic acid takes place at *meta*-position. Due to resonance in benzoic acid, there is high electron density at *meta*-position. Therefore, electrophilic substitution in benzoic acid takes place at *meta*-position.



(ii) Refer to answer 128.

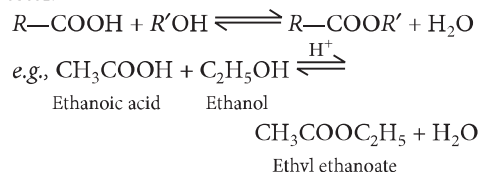


146. (i) The overall acid strength increases in the order.

4-methoxybenzoic acid < benzoic acid < 3,4-dinitrobenzoic acid.

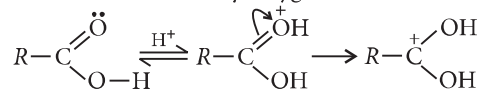
(ii) Refer to answer 135.

**147. Esterification** : Carboxylic acids react with alcohols or phenols in the presence of a mineral acid like concentrated  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  gas as catalyst and give ester.

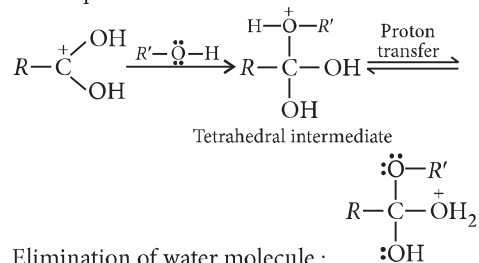


**Mechanism of esterification** : It is a nucleophilic acyl substitution.

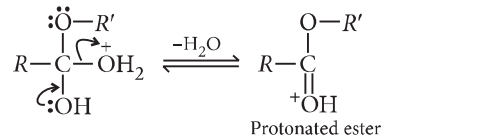
(a) Protonation of carboxyl oxygen :



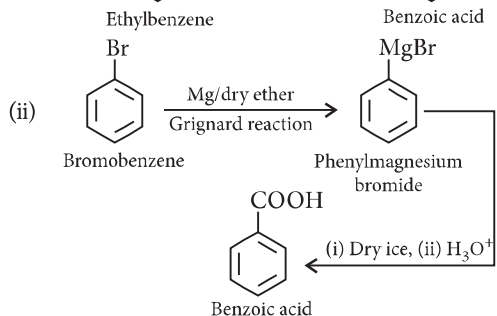
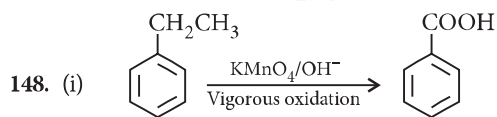
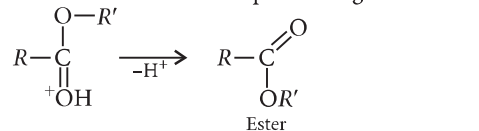
(b) Nucleophilic addition of alcohol :



(c) Elimination of water molecule :



(d) Protonated ester loses a proton to give ester :



149. (i) 4-methoxybenzoic acid < benzoic acid < 4-nitrobenzoic acid < 3,4-dinitrobenzoic acid.  
 (ii) The overall acidic strength increases in the order :  
 $(\text{CH}_3)_2\text{CHCOOH} < \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} < \text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH} < \text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$

150. (i) The strength of an acid is indicated by  $\text{p}K_a$  value, where,  $\text{p}K_a = -\log K_a$   
 Since monochloroethanoic acid is weaker than dichloroethanoic acid so it has lower value of dissociation constant  $K_a$ .  
 Therefore, it has higher value of  $\text{p}K_a$ .

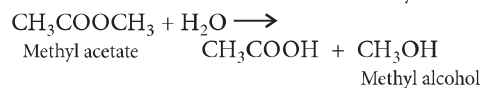
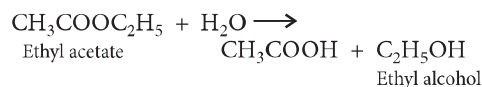
(ii) The  $-\text{COOH}$  group in benzoic acid is attached to  $sp^2$ -carbon of the phenyl ring and is more acidic than acetic acid in which  $-\text{COOH}$  group is attached to  $sp^3$ -carbon atom of  $\text{CH}_3$  group.

So, benzoic acid is stronger than acetic or acetic acid is weaker acid than benzoic acid.

151. (i) Refer to answer 126.

(ii) Refer to answer 129.

152. (i) Ethylacetate is hydrolysed slowly by water to form ethyl alcohol while methyl acetate gives methyl alcohol.

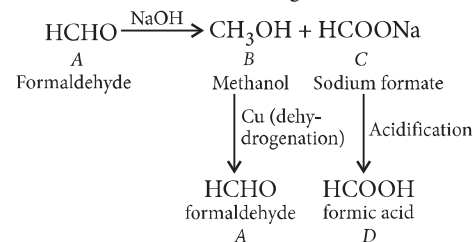


The hydrolysis product of ethyl acetate undergo iodoform test with iodine and alkali.

(ii) Refer to answer 139(b).

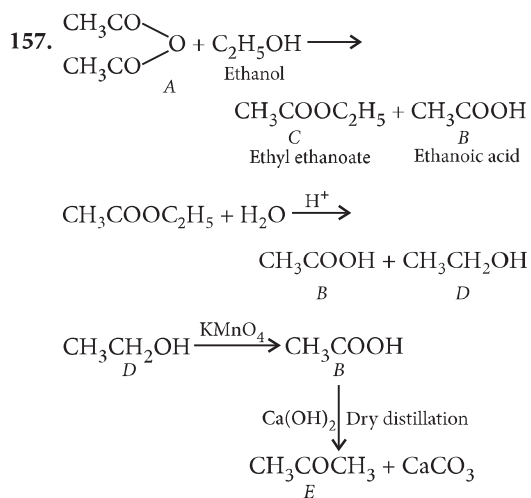
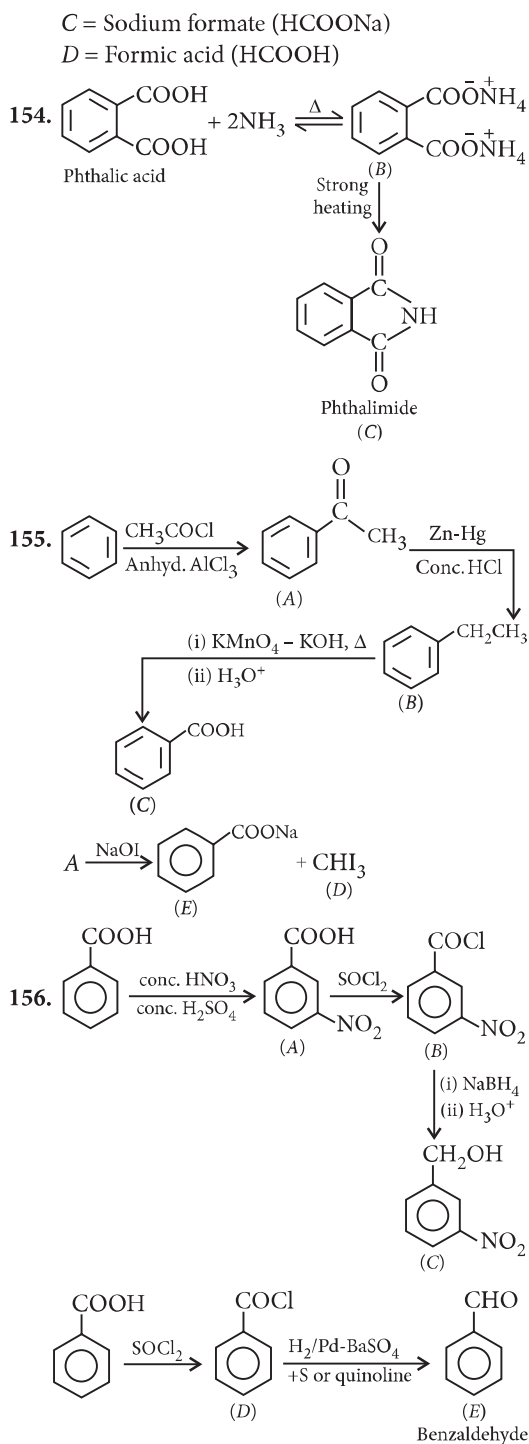
153. Since the molecular formula of *D* is  $\text{CH}_2\text{O}_2$ , thus, *D* is  $\text{HCOOH}$  (formic acid). *D* is obtained by the acidification of *C*, so, *C* is sodium formate ( $\text{HCOONa}$ ).

Thus, *A* must be formaldehyde (as it undergoes Cannizzaro reaction with a strong base).

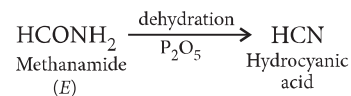
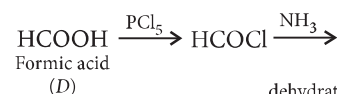
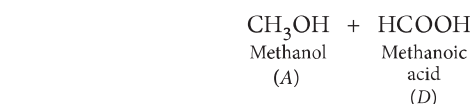
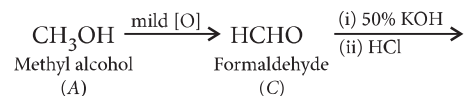
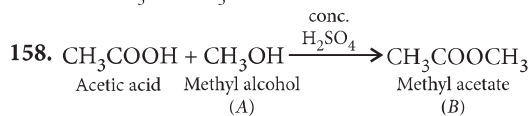
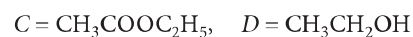


Thus, *A* = Formaldehyde ( $\text{HCHO}$ )

*B* = Methanol ( $\text{CH}_3\text{OH}$ )



*E* does not give Tollen's reagent test and does not reduce Fehling's solution as it is ketone.



Therefore, (A) : Methyl alcohol

(B) : Methyl acetate

(C) : Formaldehyde

(D) : Formic acid

(E) : Formamide

