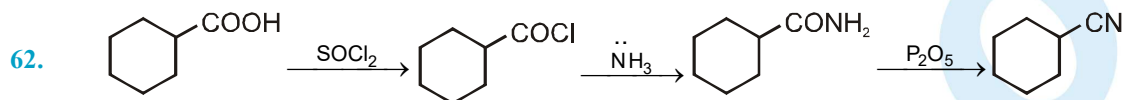
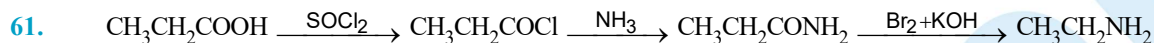
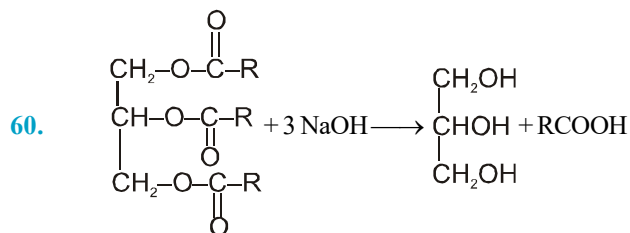


## HINTS &amp; SOLUTIONS

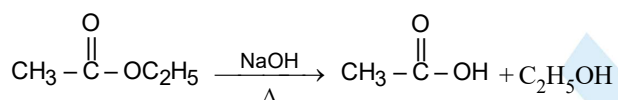
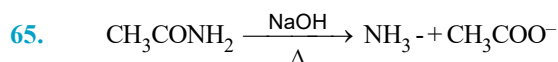
## EXERCISE - 1

## Single Choice

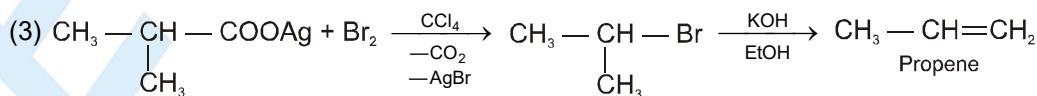
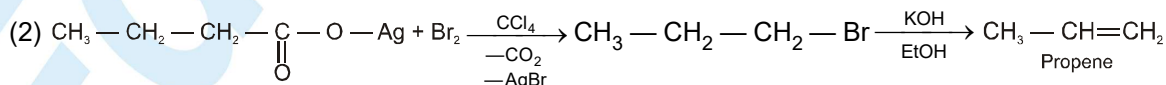
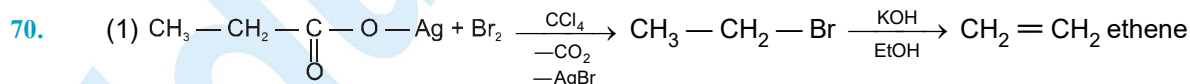
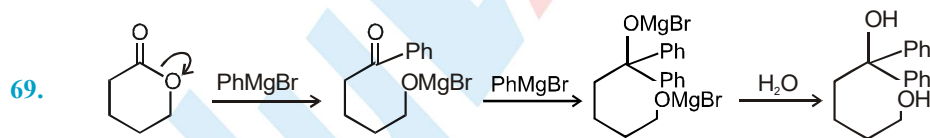
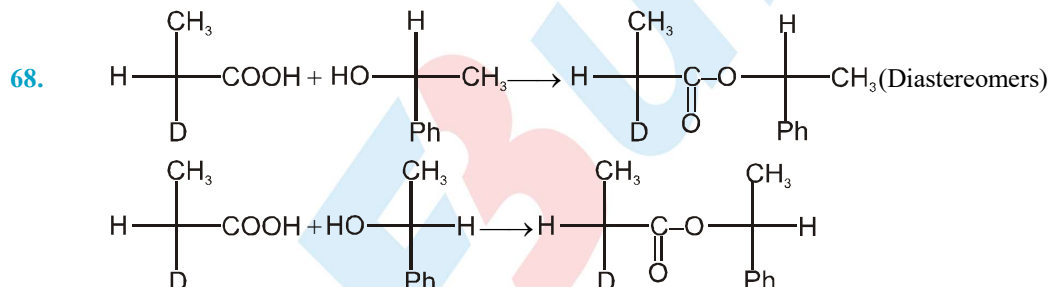
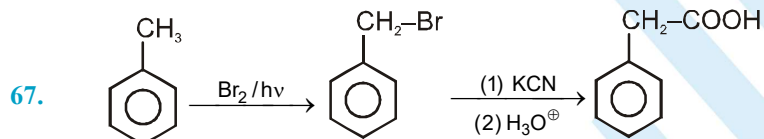
1. 
$$\text{C}_2\text{H}_5\text{Br} \xrightarrow{\text{Alc. KOH}} \text{CH}_2=\text{CH}_2 \xrightarrow[\text{CCl}_4]{\text{Br}_2} \begin{array}{c} \text{Br} \\ | \\ \text{CH}_2-\text{CH}_2 \\ | \\ \text{Br} \end{array} \xrightarrow[\text{(excess)}]{\text{KCN}} \begin{array}{c} \text{CN} \\ | \\ \text{CH}_2-\text{CH}_2 \\ | \\ \text{CN} \end{array} \xrightarrow{\text{H}_3\text{O}^+} \begin{array}{c} \text{CH}_2-\text{CH}_2-\text{COOH} \\ | \\ \text{COOH} \end{array}$$
6. 
$$\begin{array}{l} \text{Ph}-\text{CH}_3 \quad \text{Ph}-\text{COO}^- \\ \text{Ph}-\text{CH}=\text{CH}-\text{CH}_3 \xrightarrow{\text{Hot Alkaline KMnO}_4} \text{Ph}-\text{COO}^- \\ \text{Ph}-\text{C}\equiv\text{C}-\text{CH}_3 \xrightarrow{\text{Hot Alkaline KMnO}_4} \text{Ph}-\text{COO}^- \end{array}$$
7.  $\alpha$ -halogenation reaction [ $\alpha$ -H must present].
8. It is Hell Volhard Zelinsky reaction.
10. 
$$\text{HCOOH} \xrightarrow{\text{AgNO}_3+\text{NH}_4\text{OH}} \text{CO}_2 + \text{H}_2\text{O} + \text{Ag} \downarrow$$
12. 
$$\begin{array}{l} \text{RCOOH} + \text{SOCl}_2 \longrightarrow \text{RCOCl} + \text{SO}_2 + \text{HCl} \\ \text{RCOOH} + \text{PCl}_5 \longrightarrow \text{RCOCl} + \text{POCl}_3 \\ \text{RCOOH} + \text{PCl}_3 \longrightarrow \text{RCOCl} + \text{H}_3\text{PO}_3 \end{array}$$
13. Rate of decarboxylation  $\propto$  -m effect of substituent at a position.
14. 
$$\begin{array}{c} \text{O} \\ || \\ \text{CH}_2-\text{C}-\text{OH} \\ | \\ \text{CH}_2 \\ | \\ \text{C}-\text{OH} \\ || \\ \text{O} \end{array} \xrightarrow[\text{-CO}_2]{\Delta} \text{CH}_3-\text{C}-\text{OH} \quad \text{O} ||$$
21. Reactivity  $\mu$  Partial positive charge on C=O carbon.
22. 
$$\text{CH}_3\text{COONa} + \text{CH}_3\text{COCl} \longrightarrow \text{CH}_3-\text{COO}-\text{COCH}_3$$
23. 
$$\text{R}-\text{CH}_2\text{OH} + \text{RCOCl} \longrightarrow \text{R}-\text{CH}_2-\text{O}-\text{CO}-\text{R}$$
27. Electron withdrawing groups increase the rate of  $\text{S}_{\text{N}}2$ Th reaction.
28. Ester gives positive test with NaOH and phenolphthalein.
29. Saponification is a base catalysed hydrolysis ( $\text{S}_{\text{N}}2$ Th) reaction which is a sterically controlled reaction too. The least crowded ester around acyl carbon will be most reactive towards this reaction.
32. 
$$\text{C}_4\text{H}_{10}\text{O}_4 \xrightarrow{\text{Ac}_2\text{O}} \text{C}_{12}\text{H}_{18}\text{O}_8 \left[ \begin{array}{c} \text{HO}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{OH} \\ | \\ \text{OH} \end{array} \right] \xrightarrow{\text{Ac}_2\text{O}} \left[ \begin{array}{c} \text{OAc} \\ | \\ \text{AcO}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{OAc} \\ | \\ \text{OAc} \end{array} \right]$$
33. 
$$\text{Cyclohexyl-CO-OCH}_3 + \text{H}_2\text{NCH}_3 \longrightarrow \text{Cyclohexyl-CO-NH-CH}_3 + \text{CH}_3\text{OH}$$
34. 
$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2 \xrightarrow[\Delta]{\text{NaOH}} \text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^- \xrightarrow{\text{HCl}} \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{NH}_4\text{Cl}$$



64. HVZ reaction.



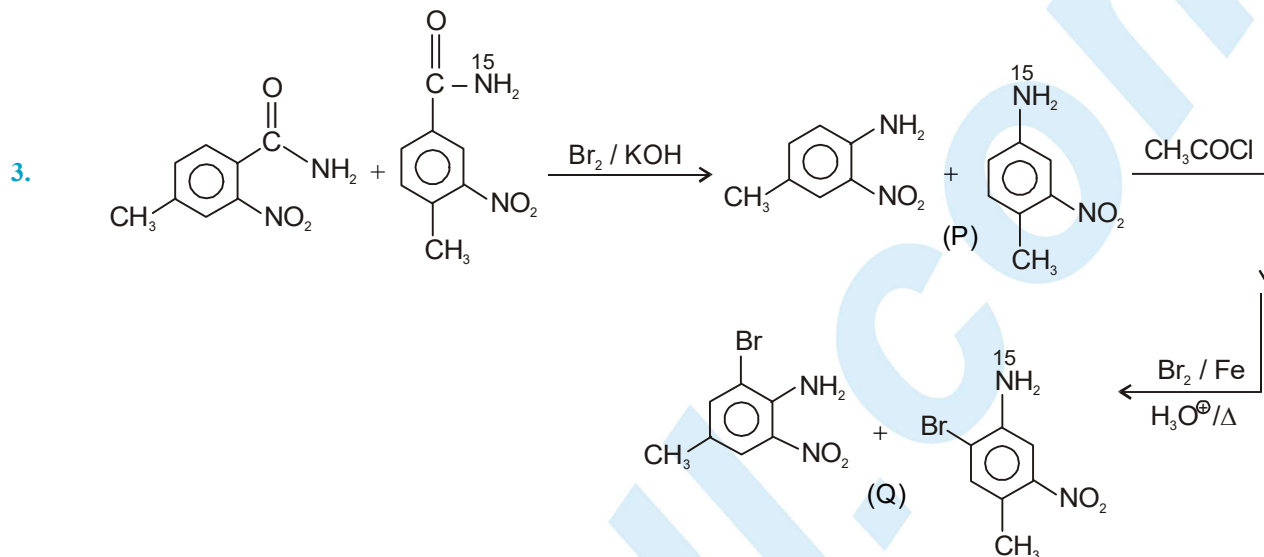
66. In fumaric acid both COOH groups are present on opposite side so it is unaffected on heating.



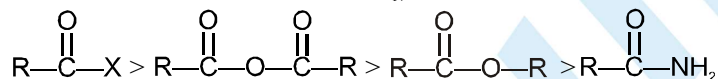
71. Acidic strength  $\propto$  stability of anion  
 $\propto -I$  and  $-M$  group

EXERCISE - 2

Part # I : Multiple Choice



4. Hydrolysis of acid derivative is an  $S_N2$  reaction and the reactivity of acid derivatives towards  $S_N2$  is

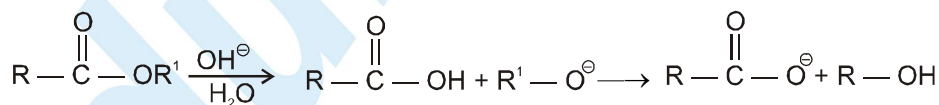
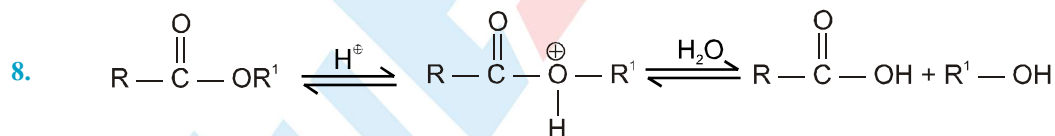


5. It is Fischer esterification reaction.



Part # II : Assertion & Reason

7.  $S_N2$  is a sterically as well as electronically controlled reaction i.e., steric crowding around acyl carbon decreases rate of reaction and increase in +ve charge centre around acyl carbon increases rate of reaction:



Nucleophilic attack is difficult.

13. Boiling point a molecular mass  $\propto$  intermolecular H-bonding.  
 Thus p-hydroxybenzoic acid is having more bp than o-hydroxybenzoic acid (intramolecular H-bonding).

EXERCISE - 3

Part # I : Matrix Match Type

4. (1)  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}' \xrightarrow{\text{OH}^-} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}^--\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}' \longrightarrow \text{R}-\text{N}=\text{C}=\text{O}$   
Lossen reaction
- (2)  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl} \xrightarrow{(i) \text{NaN}_3 / \Delta} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}^--\text{N}^+\equiv\text{N} \longrightarrow \text{R}-\text{N}=\text{C}=\text{O}$   
Curtius reaction
- (3)  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2 \xrightarrow{\text{Br}_2 / \text{OH}^-} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{Br} \xrightarrow{\text{OH}^-} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}^--\text{Br} \longrightarrow \text{R}-\text{N}=\text{C}=\text{O}$   
Hoffman
- (4)  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} + \text{N}_3\text{H} \xrightarrow{\text{Schmidt reaction}} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}^--\text{N}^+\equiv\text{N} \longrightarrow \text{R}-\text{N}=\text{C}=\text{O}$
5. (A) It will be an acid base reaction.  
(B) it is an acid catalysed esterification.  
(C) it is an acid catalysed hydrolysis.  
(D) It is a base catalysed hydrolysis which is also known as saponification

Part # II : Comprehension

Comprehension # 1 :

- Hoffmann rearrangement is shown by 1° amide only.
- Rate of reaction in hoffmann rearrangement among different amide depends on migratory aptitude of group in the amide.
- Hoffmann rearrangement is 100% intramolecular. one amide will give only one amine with  $\text{Br}_2/\text{OH}^\ominus$ .

Comprehension # 2 :

- Z is  $\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{COOH}$
- X is an anion and it has no acidic hydrogen.
- any mono substituted benzene oxidises to benzoic acid.

Comprehension # 3 :

1.  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} \xrightarrow{\text{H}^\oplus} \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}_2^\oplus \xrightarrow{\text{C}_2\text{H}_5\text{OH}(\Delta^\circ)} \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{18}{\text{C}}_2\text{H}_5$
- $(\text{CH}_3)_3\text{C}-\text{OH} \xrightarrow{\text{H}^\oplus} (\text{CH}_3)_3\text{C}^\oplus + \text{H}_2\text{O}^{18} \xrightarrow{\text{CH}_3\text{COOH}} (\text{CH}_3)_3\text{C}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$
2.  $\text{CH}_3-\text{COOH} + \text{D}-\underset{\text{CH}_3}{\overset{\text{H}}{\text{C}}}-\text{OH} \longrightarrow \text{D}-\underset{\text{CH}_3}{\overset{\text{H}}{\text{C}}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$   
(1°) optically active
- $\text{CH}_3-\text{COOH} + \text{Ph}-\underset{\text{C}_2\text{H}_5}{\overset{\text{CH}_3}{\text{C}}}-\text{OH} \longrightarrow \text{Ph}-\underset{\text{C}_2\text{H}_5}{\overset{\text{CH}_3}{\text{C}}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$   
(3° & benzylic) racemic mixture

3. Since (+) Octan-2-ol racemises on reaction with acetic acid, therefore it must have gone through an  $\text{S}_{\text{N}}1$  reaction i.e., type II reaction.

# CARBOXYLIC ACID AND THEIR DERIVATIVES

## EXERCISE - 4

### Subjective Type

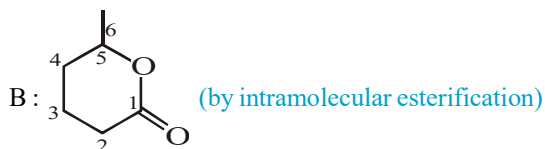
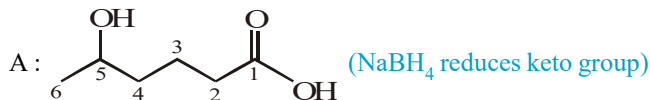
1 (A)  $\text{CH}_2\text{FCO}_2\text{H}$

(B)  $\text{CH}_2\text{ClCO}_2\text{H}$

(C)  $\text{CH}_3\text{CH}_2\text{CHFCO}_2\text{H}$



2.



3.

<sup>18</sup>O is in ester  $\text{CH}_3\text{COCH}_2\text{CH}_3$

4.

Formate ion shows equivalent resonating structures while formic acid does not.

5.

After the first dissociation, maleate ion is more stabilised due to intramolecular H-bonding, whereas fumarate ion does not have intramolecular H-bonding.

6.

(A)  $\text{NH}_2^-$

(B)  $\text{CH}_3^-$

(C)  $\text{CH}_3\text{COO}^-$

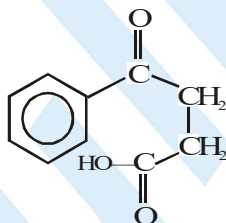
(D)  $\text{CCl}_3\text{COO}^-$

7.

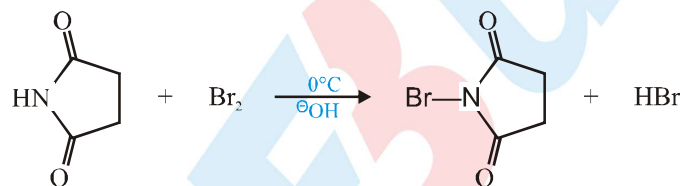
I:  $\text{LiAlH}_4$  II:  $\text{Pd/BaSO}_4$  (Rosenmund)

8.

A is formed by Friedel-Crafts reaction A:



9.

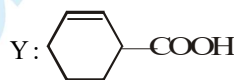


1-Bromopyrrolidine-2, 5-dione  
or N-Bromosuccinimide (NBS)

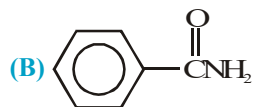
It is used for brominating in allylic and benzylic hydrogen.



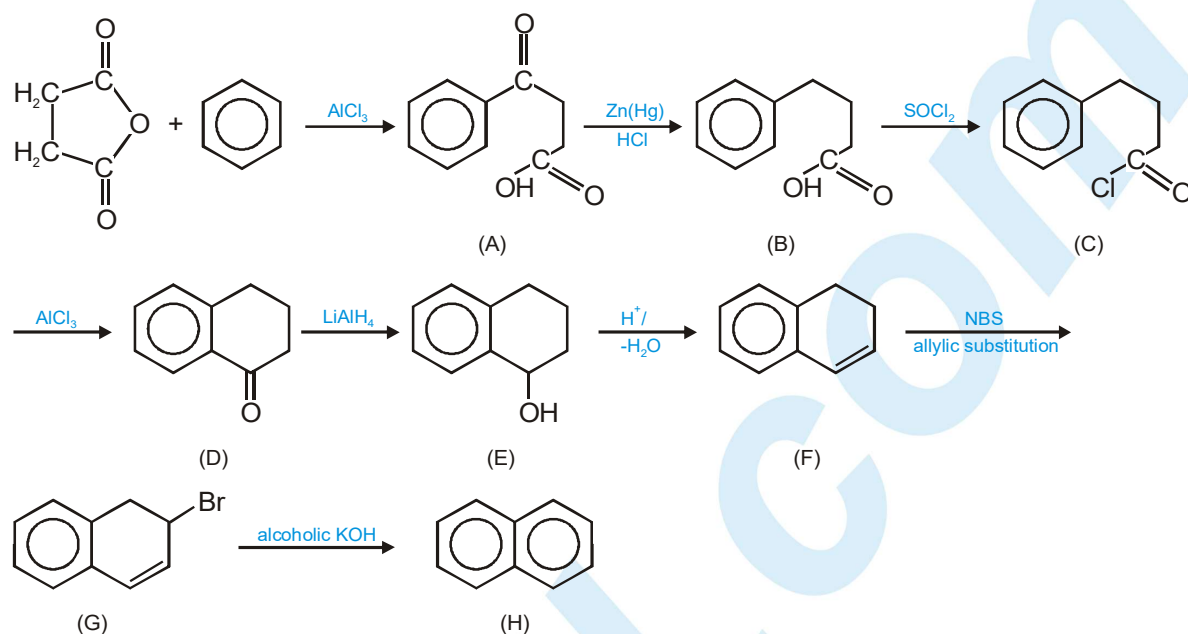
10.



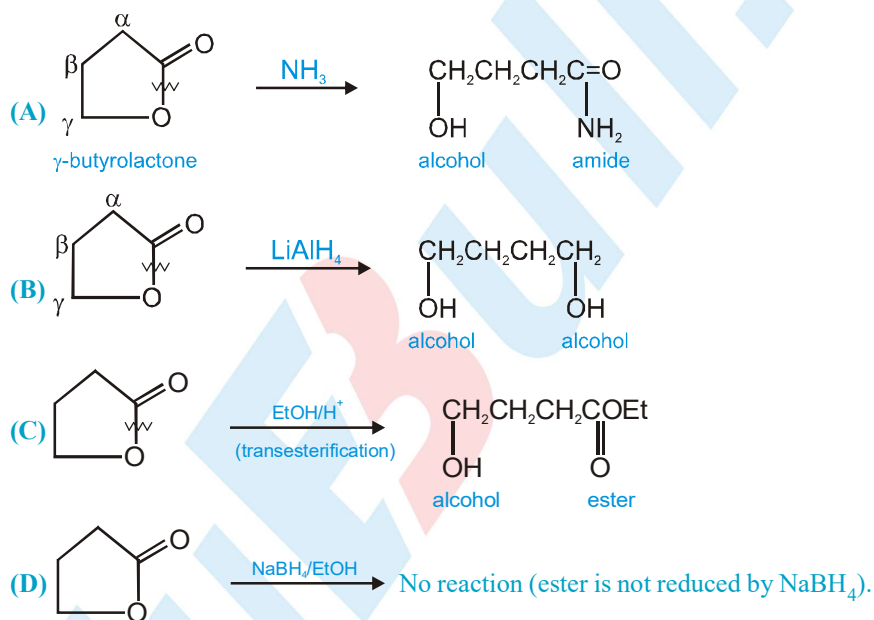
11.



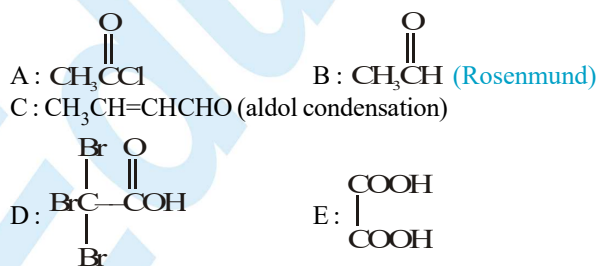
12.



13.



14.

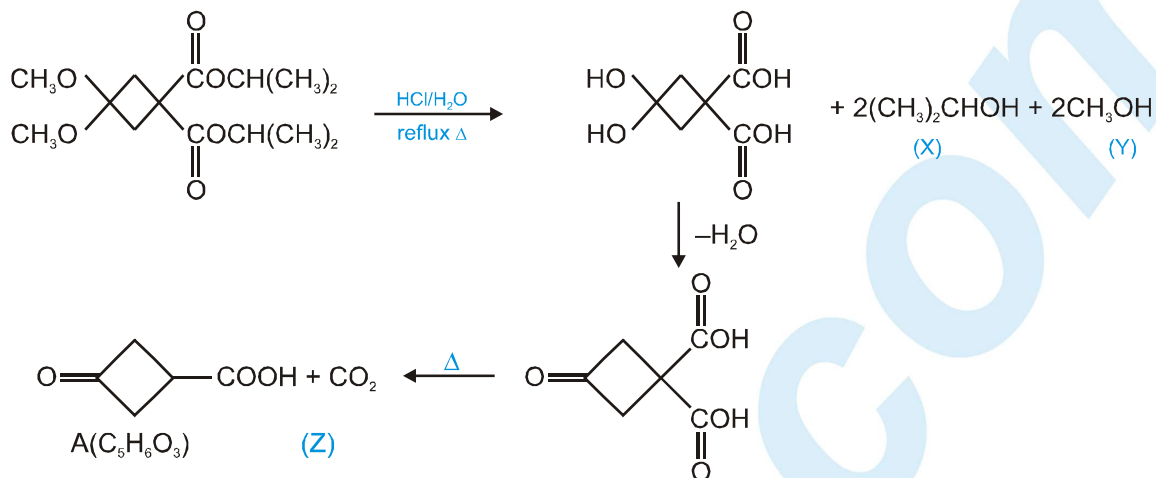
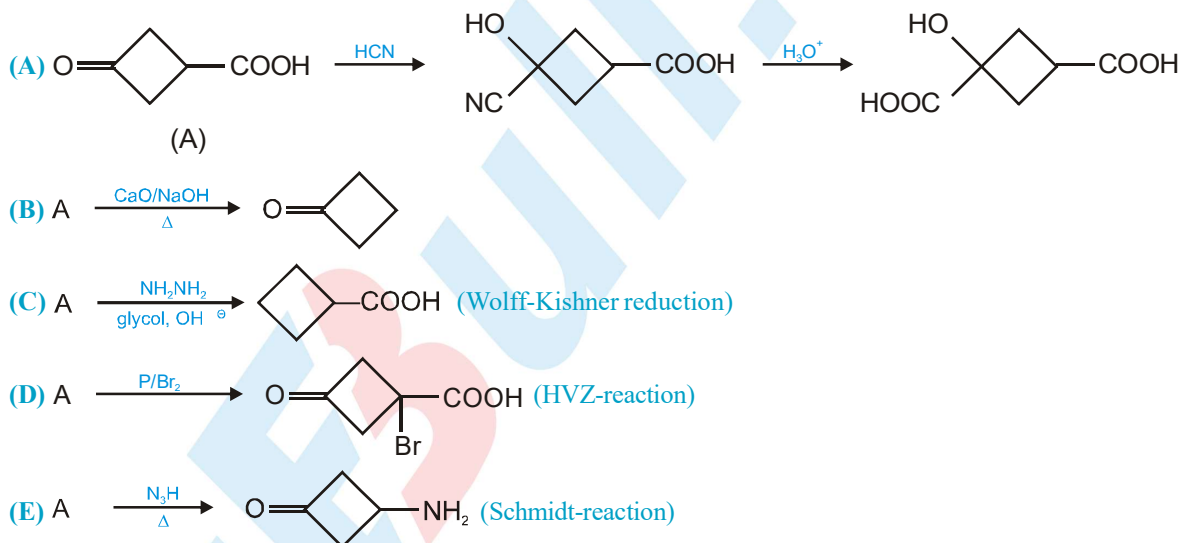


15.

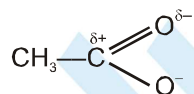
Given compound represents

(i) acetal (ii) ester

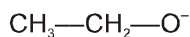
When it is subjected to acidic hydrolysis, acetal changes to carbonyl group and ester changes to acid.


 (X), (Y) and (Z) are thus, other carbon containing product along with  $\text{C}_5\text{H}_6\text{O}_3$  which is the main product.  $\text{A}(\text{C}_5\text{H}_6\text{O}_3)$  has (i) keto group (ii) carboxylic group


16.

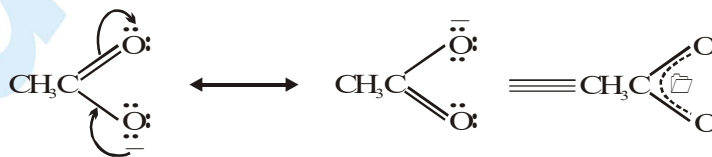


Acetate ion



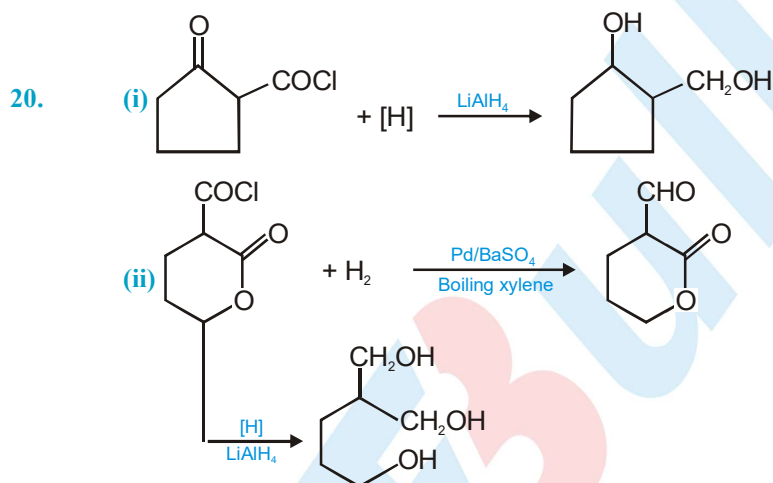
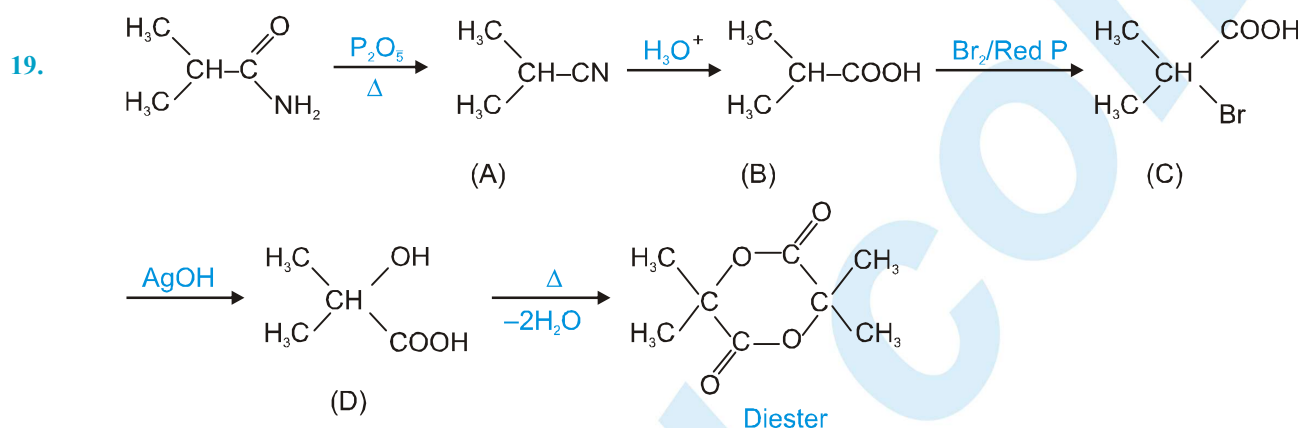
Ethoxide

Electron delocalation, as shown by following resonance structures, causes the negative charge in acetate to be shared equally by both oxygens. This type of resonance effect is not possible in ethoxide ion.



17. In case of carbonyl compounds  $\text{H}^-$  or  $\text{R}^-$  are poor leaving group, therefore addition take place. But in case of acid derivatives,  $\text{Z}^-$  are good leaving group therefore substitution take place.

18. (i) A:  $\text{CH}_3\text{—NH}_2$       B:  $\text{CH}_3\text{—}\overset{\text{O}}{\parallel}\text{C—NH}_2$   
(ii) Reagent =  $\text{Br}_2/\text{Alc. KOH}$



- 21.** Benzoic acid and Ethyl benzoate can be distinguished by sodium bicarbonate test.

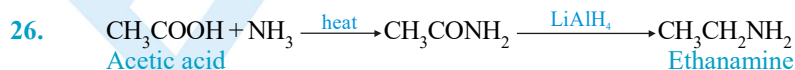
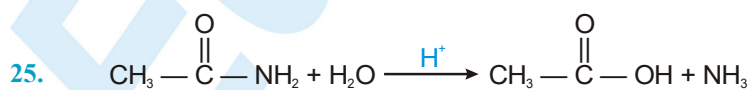
### Sodium bicarbonate test :

Acids react with  $\text{NaHCO}_3$  to produce brisk effervescence due to the evolution of  $\text{CO}_2$  gas. Benzoic acid being an acid responds to this test, but ethylbenzoate does not.


$$\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5 + \text{NaHCO}_3 \longrightarrow \text{No effervescence due to evolution of CO}_2 \text{ gas.}$$

22. Ethylamine salt and methanoic acid

23.  $\text{p-O}_2\text{NC}_6\text{H}_4\text{COCl} > \text{PhCOCl} > \text{p-CH}_3\text{OC}_6\text{H}_4\text{COCl}$ .



## CARBOXYLIC ACID AND THEIR DERIVATIVES

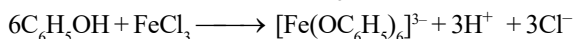
27.  $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{COOH}$  has least  $-\text{I}$  group and hence smallest acid dissociation constant.
28. Electron-donating groups decrease the strengths of acids, while electron-withdrawing groups increase the strengths of acids. As methoxy group is an electron-donating group, 4-methoxybenzoic acid is a weaker acid than benzoic acid. Nitro group is an electron-withdrawing group and will increase the strengths of acids. As 3,4-dinitrobenzoic acid contains two nitro groups, it is a slightly stronger acid than 4-nitrobenzoic acid. Hence, the strengths of the given acids increase as :

3,4-Dinitrobenzoic acid > 4-Nitrobenzoic acid > Benzoic acid > 4-Methoxybenzoic acid.

29. Phenol and benzoic acid can be distinguished by ferric chloride test.

### Ferric chloride test :

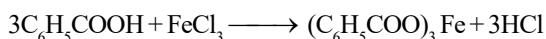
Phenol reacts with neutral  $\text{FeCl}_3$  to form an iron-phenol complex giving violet colouration



Phenol

Iron-phenol complex  
(Violet colour)

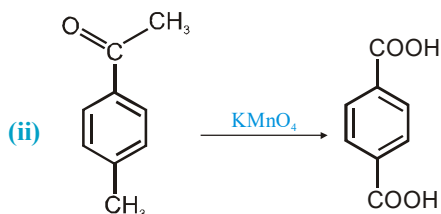
But benzoic acid reacts with neutral  $\text{FeCl}_3$  to give a buff coloured ppt. of ferric benzoate



Benzoic acid

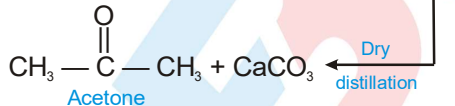
Ferric benzoate  
(Buff coloured ppt)

30. (i)  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH} \xrightarrow{\text{KMnO}_4} \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{COOH}$

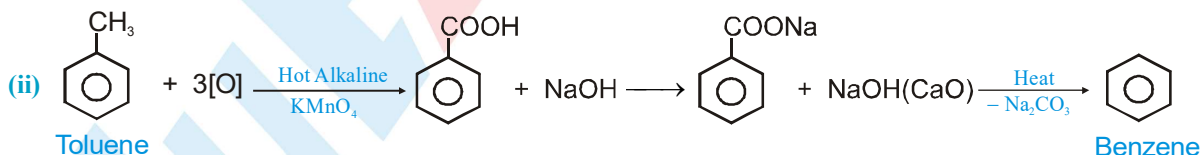


31. (i)  $2\text{CH}_3\text{COOH} \xrightarrow{\text{Ca}(\text{OH})_2} \text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{Ca}-\text{O}-\text{C}(=\text{O})-\text{CH}_3$

Acetic acid



Acetone



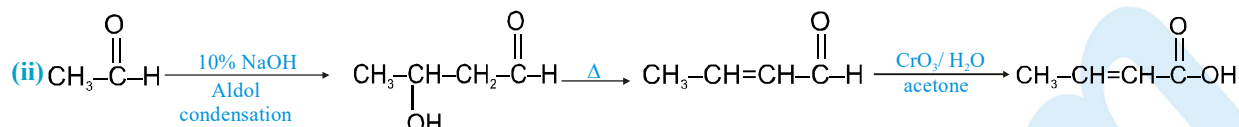
Toluene

Benzene

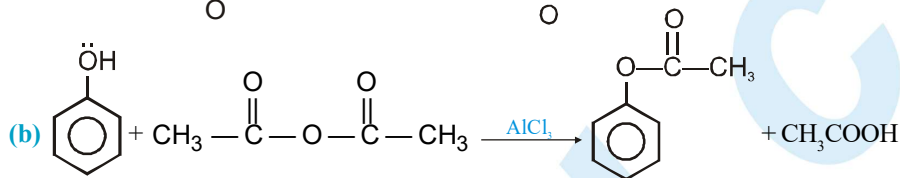
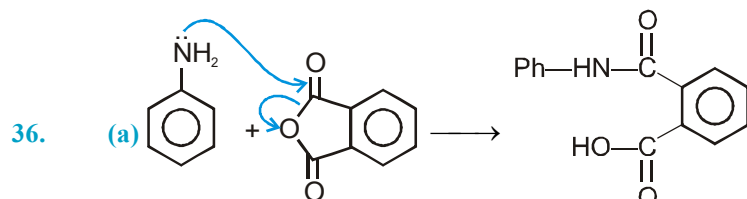
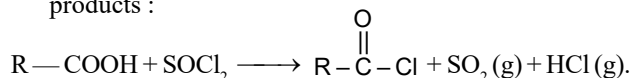
32. (a)  $2\text{CH}_3-\text{C}(=\text{O})-\text{OH} \xrightarrow[\text{heat}]{\text{P}_2\text{O}_5} \text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-\text{CH}_3 + \text{H}_2\text{O}$
- (b)  $\text{CH}_3-\text{C}(=\text{O})-\text{OH} + \text{PCl}_5 \longrightarrow \text{CH}_3\text{COCl} + \text{POCl}_3 + \text{HCl}$

33. As the size of the substituents on the  $\alpha$  C increases, the tetrahedrally bonded intermediate becomes more crowded. The greater the crowding, the larger is  $\Delta H^\ddagger$  of the TS and the slower is the reaction.

34. (i)  $\text{H}-\text{C}\equiv\text{C}-\text{H} \xrightarrow[\text{H}_2\text{SO}_4]{\text{HgSO}_4} \text{CH}_3-\text{C}(=\text{O})-\text{H} \xrightarrow[\Delta]{\text{KMnO}_4} \text{CH}_3-\text{COOH}$



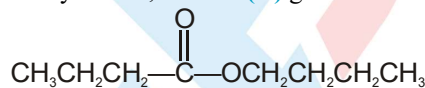
35. (a)  $\text{PCl}_3$ ,  $\text{PCl}_5$  &  $\text{SOCl}_2$   
 (b)  $\text{SOCl}_2$  because the by products of the reaction are the gases  $\text{SO}_2$  and  $\text{HCl}$  which are easily separated from the products :



37.  $\text{RCOOH} + \text{R}'\text{OH}$   
 Carboxylic acid Alcohol

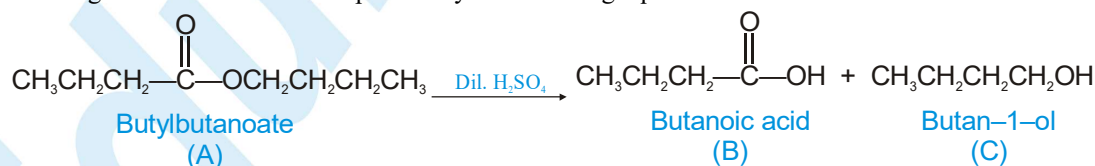
If either water or ester is not removed as soon as it is formed, then it reacts to give back the reactants as the reaction is reversible. Therefore, to shift the equilibrium in the forward direction i.e., to produce more ester, either of the two should be removed.

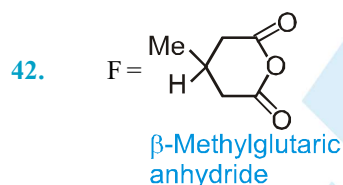
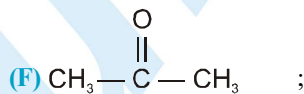
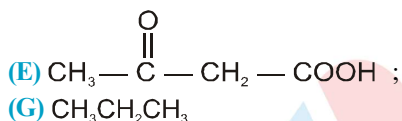
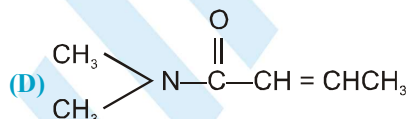
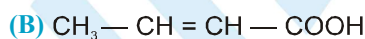
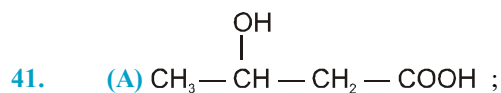
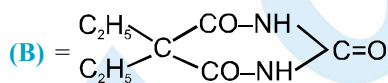
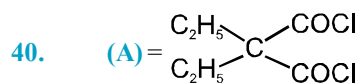
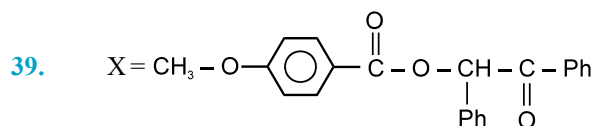
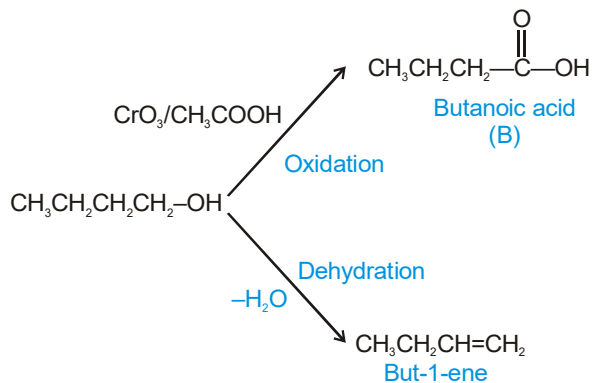
38. An organic compound (A) with molecular formula  $\text{C}_8\text{H}_{16}\text{O}_2$  gives a carboxylic acid (B) and an alcohol (C) on hydrolysis with dilute sulphuric acid. Thus, compound (A) must be an ester. Further, alcohol (C) gives acid (B) on oxidation with chromic acid. Thus, (B) and (C) must contain equal number of carbon atoms. Since compound (A) contains a total of 8 carbon atoms, each of (B) and (C) contain 4 carbon atoms. Again, on dehydration, alcohol (C) gives but-1-ene. Therefore, (C) is of straight chain and hence, it is butan-1-ol.



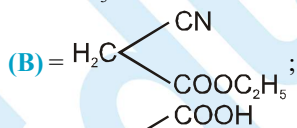
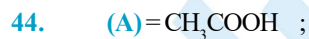
Butylbutanoate

All the given reactions can be explained by the following equations.

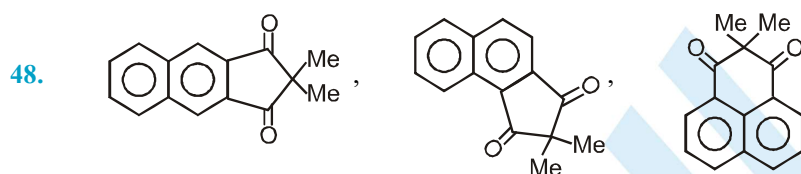
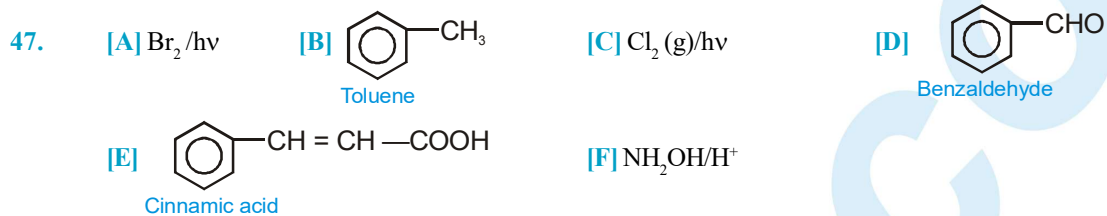
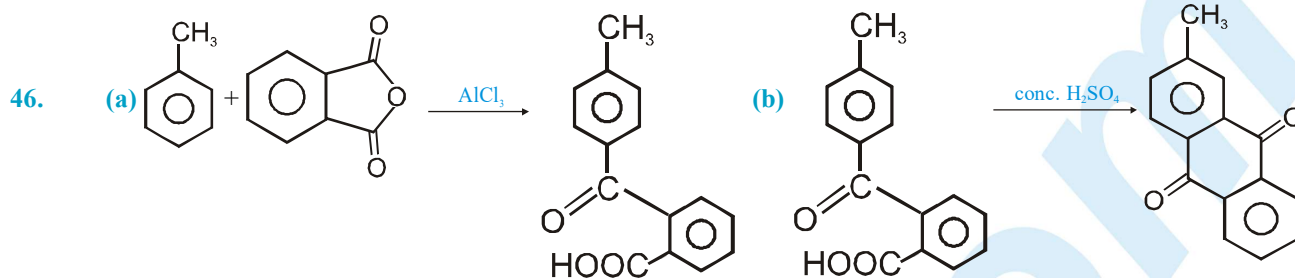




43. The anhydride formed from the trans-dicarboxylic acid must have a trans fusion of two rings. There is too much strain while both ring are five-membered.



45. 6(I, II, III, V, VII & X)

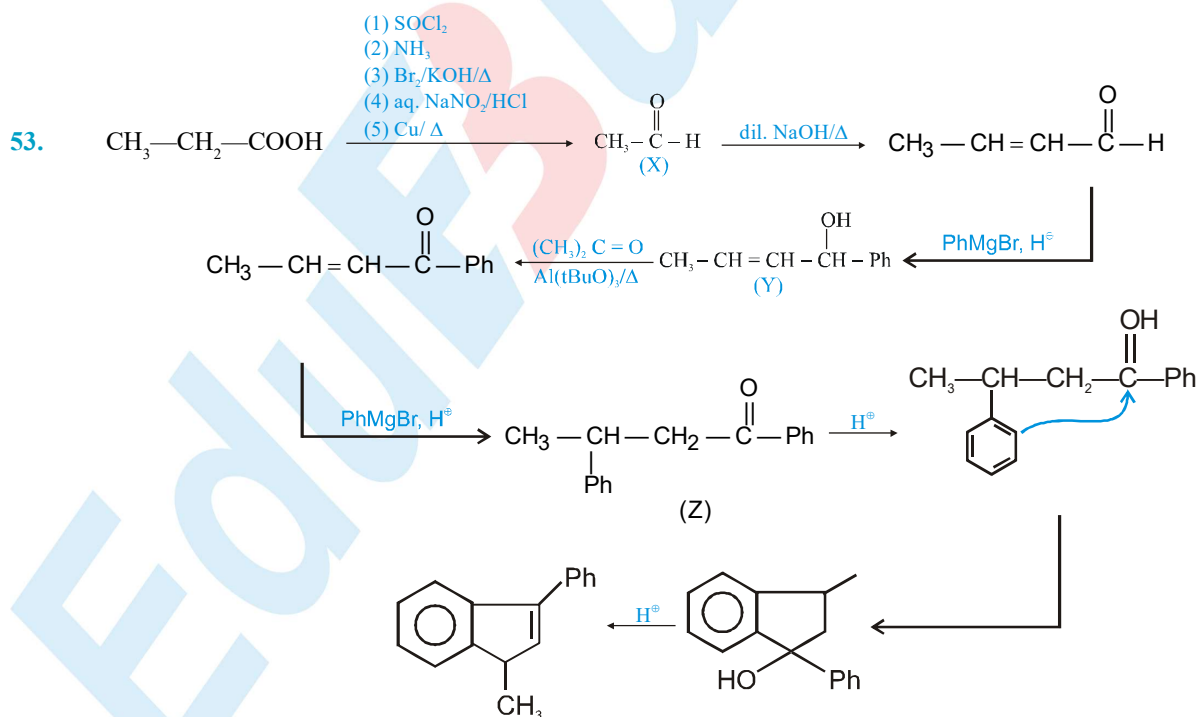


49. Dimethylacetamide lacks a H on N for intermolecular H-bonding; thus its bp is lowest, its highest molecular weights notwithstanding. Acetamide has two H's and is extensively H-bonded resulting in the highest bp, while methylacetamide has only one H and less H-bonding.

50. (I)  $x < y$  (II)  $y < z$  (III)  $x < z$

51. 2

52. First, anion of Malonic ester is formed which attacks as a nucleophile on the other reagent.

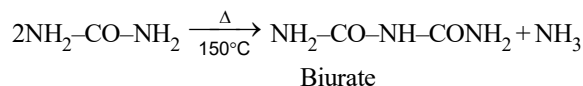


# CARBOXYLIC ACID AND THEIR DERIVATIVES

## EXERCISE - 5

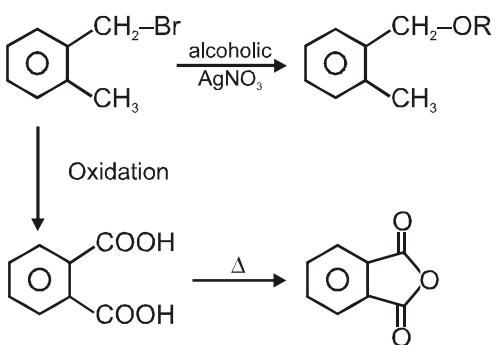
### Part # I : AIEEE/JEE-MAIN

5. The empirical formula from given percentage data is  $\text{N}_2\text{H}_4\text{CO}$ . Urea on heating gives biurate & ammonia. Biurate gives violet colour with  $\text{CuSO}_4$  solution.



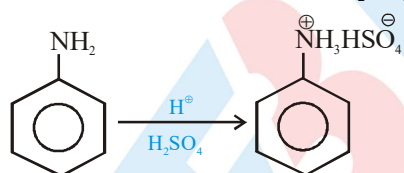
6.  $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$   
Ester (Fruity smell)

7.  $\text{CH}_3\text{COCl} \xrightarrow{\text{C}_2\text{H}_5\text{O}^-} \text{CH}_3\text{COOC}_2\text{H}_5 + \text{Cl}^-$   
Ethylethanoate

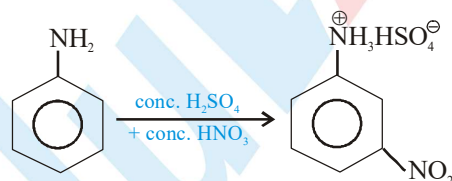
9. 

(Phthalic anhydride)

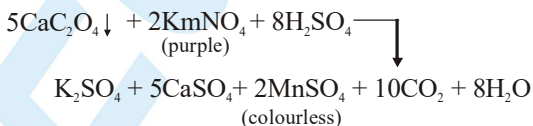
12. (i) Nitration is carried out in presence of concentrated  $\text{HNO}_3$  + concentrated  $\text{H}_2\text{SO}_4$ .  
(ii) Aniline acts as base. In presence of  $\text{H}_2\text{SO}_4$  its protonation takes place and anilinium ion is formed



- (iii) Anilinium ion is strongly deactivating group and meta directing in nature so it give meta nitration product in significant amount.



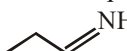
13.  $\text{Na}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4 \xrightarrow{\text{conc.}} \text{Na}_2\text{SO}_4 + \text{CO} \uparrow + \text{CO}_2 \uparrow + \text{H}_2\text{O}$

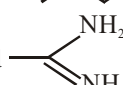



14. DIABL – H is electrophilic reducing agent reduces cynide, esters, lactone, amide, carboxylic acid into corresponding Aldehyde (partial reduction)


15. Kjeldahl's is suitable for Aniline. This method is used for quantitative analysis of N compound in organic substance ( $\text{NH}_3/\text{NH}_4^+$ ).

16. Order of base nature depends on electron donation tendency.

In compound  nitrogen is  $\text{sp}^2$  hybridized so least basic among all given compound.

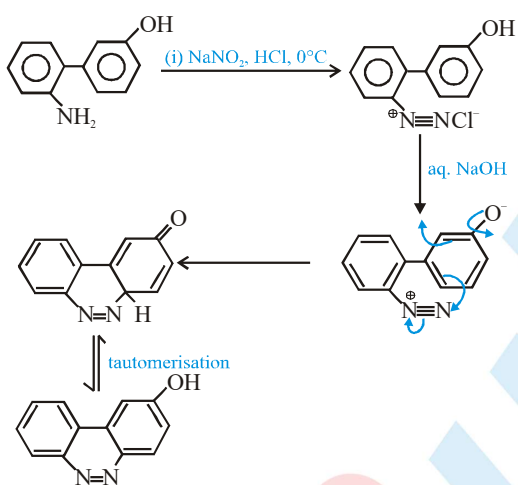
compound  is very strong nitrogenous organic base as lone pair of one nitrogen delocalize in resonance and make another nitrogen negatively charged and conjugate acid have two equivalent resonating structure. Thus it is most basic in given compounds.

  $\text{NHCH}_3$  (secondary amine) more basic than

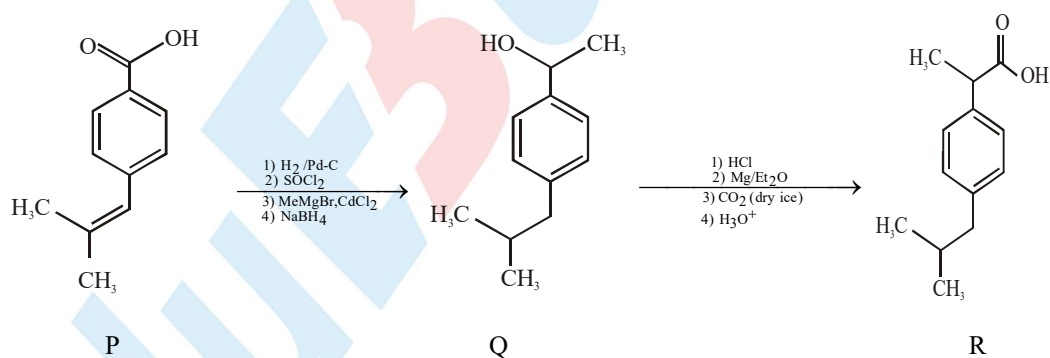
  $\text{NH}_2$  (primary amine)

Part # II : IIT-JEE ADVANCED

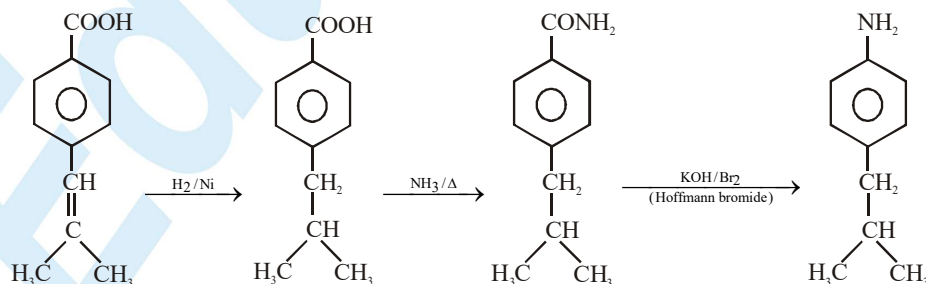
- 15.

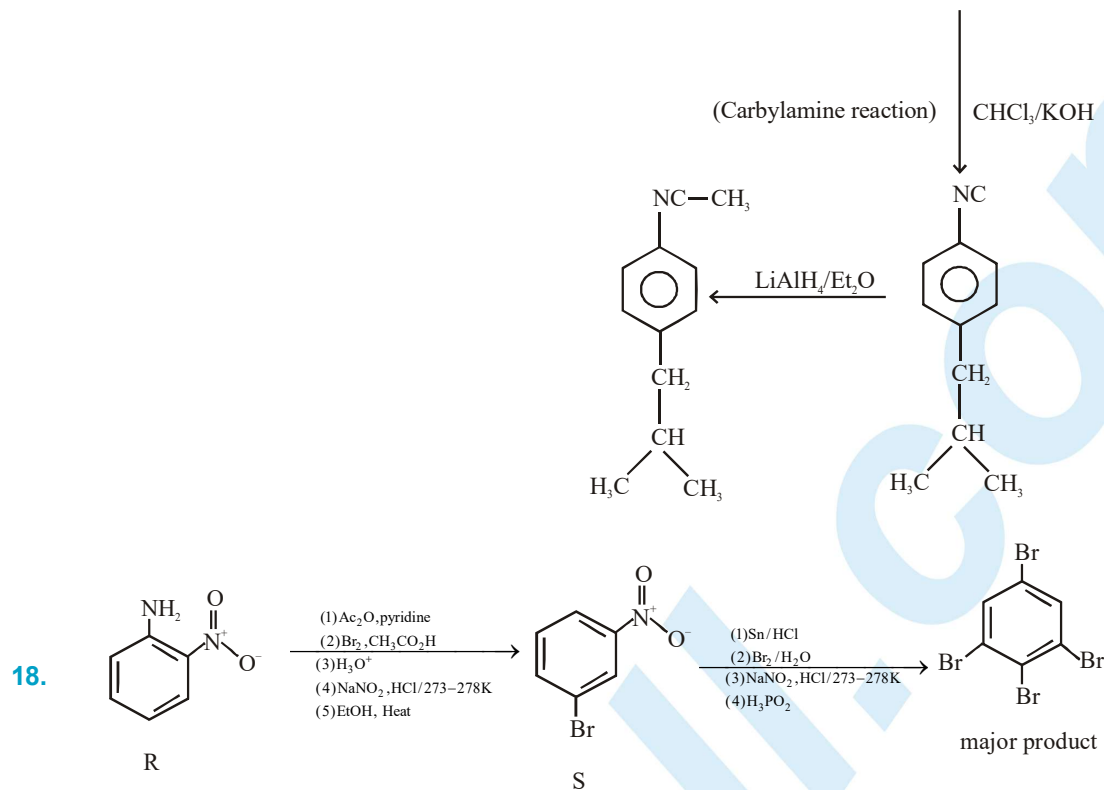


- 16.



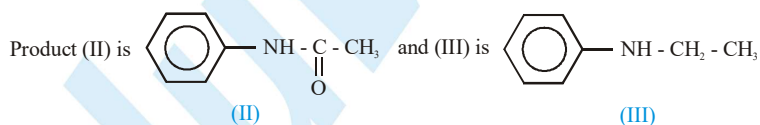
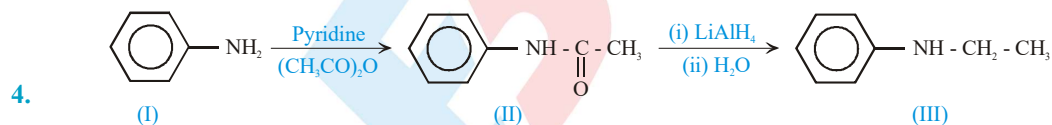
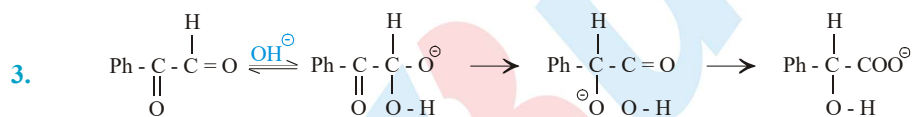
- 17.



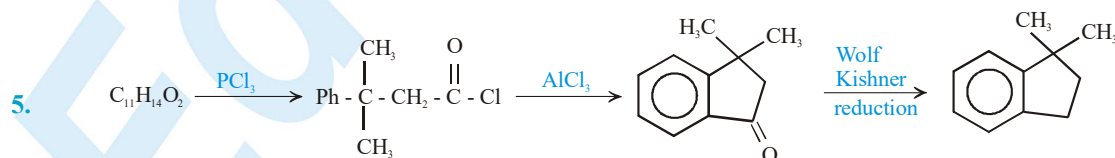


## MOCK TEST

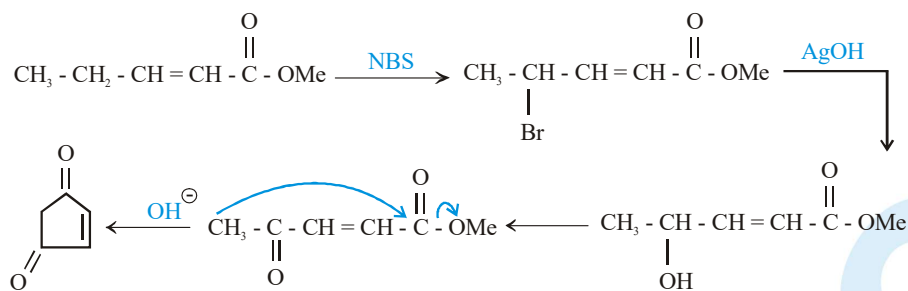
1. PhCOOH dissolves in aq.  $\text{NaHCO}_3$  solution.  
 2. Cl has more -I and less +M effect.



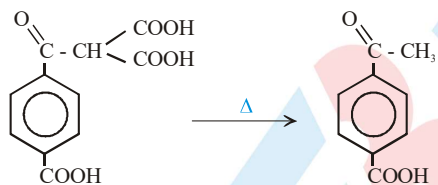
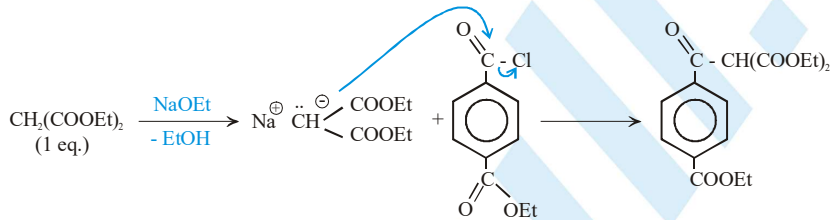
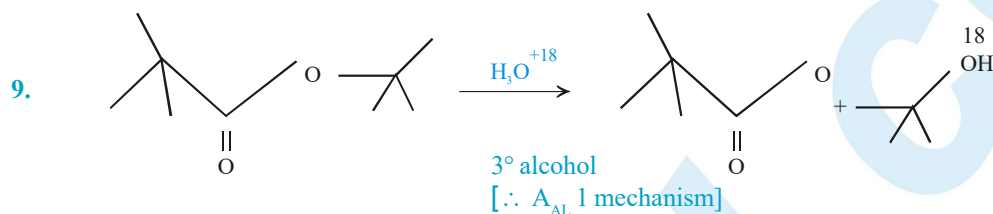
$\therefore \text{III} > \text{I} > \text{II}$  as +I effect of increases the basic strength and  $-\text{COCH}_3$  by -R, -I reduces the basic strength.



7. NBS also brominates unsaturated esters.



8. Unhindered ketone is reduced by  $[\text{LiAl}(\text{t BuO})_3 \text{H}]$



12. β - keto acid decarboxylate readily