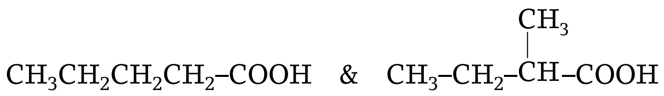
CHAPTER 4

Carboxylic Acids and its Derivatives

INTRODUCTION

Carboxylic Acids

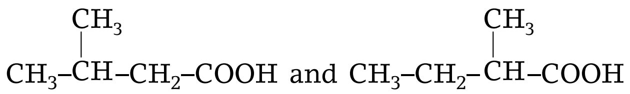
- Saturated monocarboxylic acids have general formula, $C_nH_{2n+1}COOH$ or $C_nH_{2n}O_2$.
- The carboxylic carbon and the two oxygen atoms in carboxylic acid are sp^2 hybridised.
- The C–O (single bond) of carboxylic group is shorter (1.36 Å) than normal C–O single bond (1.43 Å) in alcohols and ethers, due to resonance.
- The C=O double bond in carboxylic group is slightly longer (1.23 Å) than the normal C=O double bond (1.20 Å) in ketones and aldehyde.
- Carboxylic acid exhibits isomerism as illustrated below:
  - **(a) Chain isomerism:**



$CH_3CH_2CH_2CH_2{-}COOH$ & $CH_3{-}CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}COOH$

pentanoic acid   2-Methyl butanoic acid

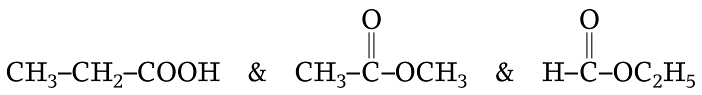
  - **(b) Position isomerism:**



$CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}CH_2{-}COOH$ and $CH_3{-}CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}COOH$

3-Methyl butanoic acid   2-Methyl butanoic acid

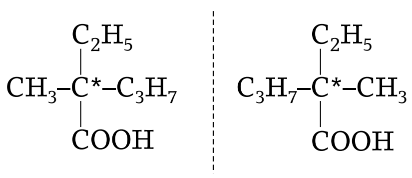
  - **(c) Functional isomerism:**



$CH_3{-}CH_2{-}COOH$ & $CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OCH_3$ & $H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OC_2H_5$

propionic acid   Methyl acetate   Ethyl formate

  - **(d) Optical isomerism:**



$CH_3{-}\underset{\underset{\displaystyle COOH}{|}}{\overset{\overset{\displaystyle C_2H_5}{|}}{C^*}}{-}C_3H_7$ ⋮ $C_3H_7{-}\underset{\underset{\displaystyle COOH}{|}}{\overset{\overset{\displaystyle C_2H_5}{|}}{C^*}}{-}CH_3$

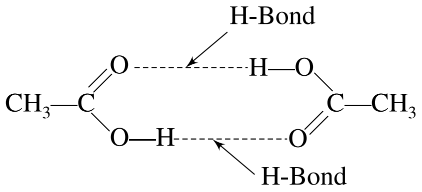
2-Ethyl-2-methyl pentanoic acid

  - **(e) Geometrical isomerism:**

cis-But-2-enoic acid   *tras*-But-2-enoic acid

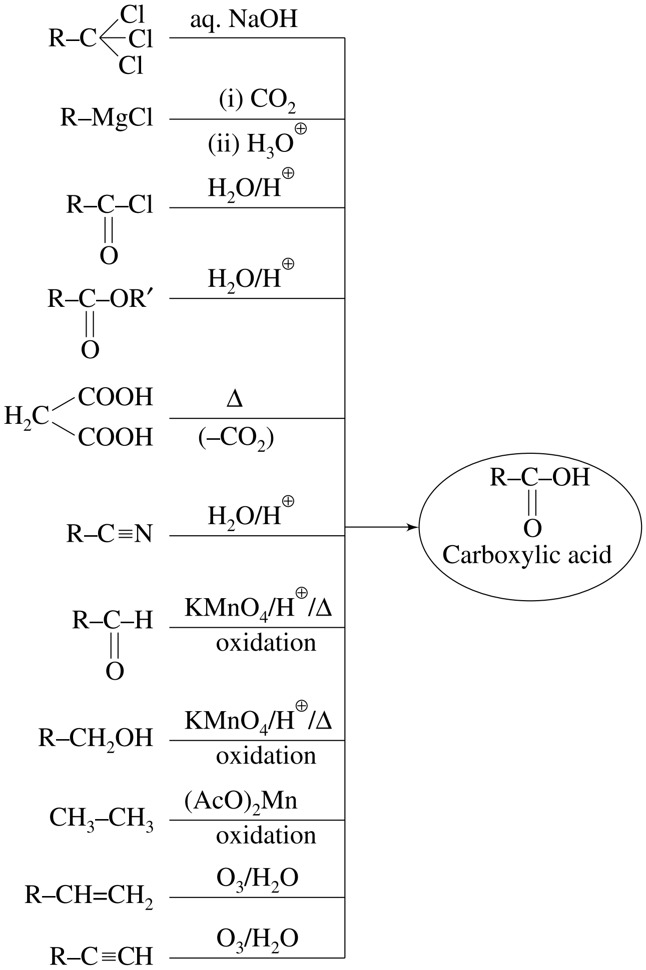
PHYSICAL PROPERTIES

- Fatty acids upto C_{10} are colourless liquid. The higher ones are colourless waxy solids.
- The first three members have a sharp pungent odour but the middle ones C_4–C_9 have the smell of rancid butter, whereas higher members are odourless.
- Lower members are completely miscible with water because of the formation of the hydrogen bonds. However, solubility decreases with increasing molecular weight because of increased effect of non-polar long carbon chain which results in weak H-bonding or no H-bonding.
- Boiling point of carboxylic acids increases regularly with increase in molecular weight. B.P. of R–COOH > R–OH due to hydrogen bonding and they exist as dimer.

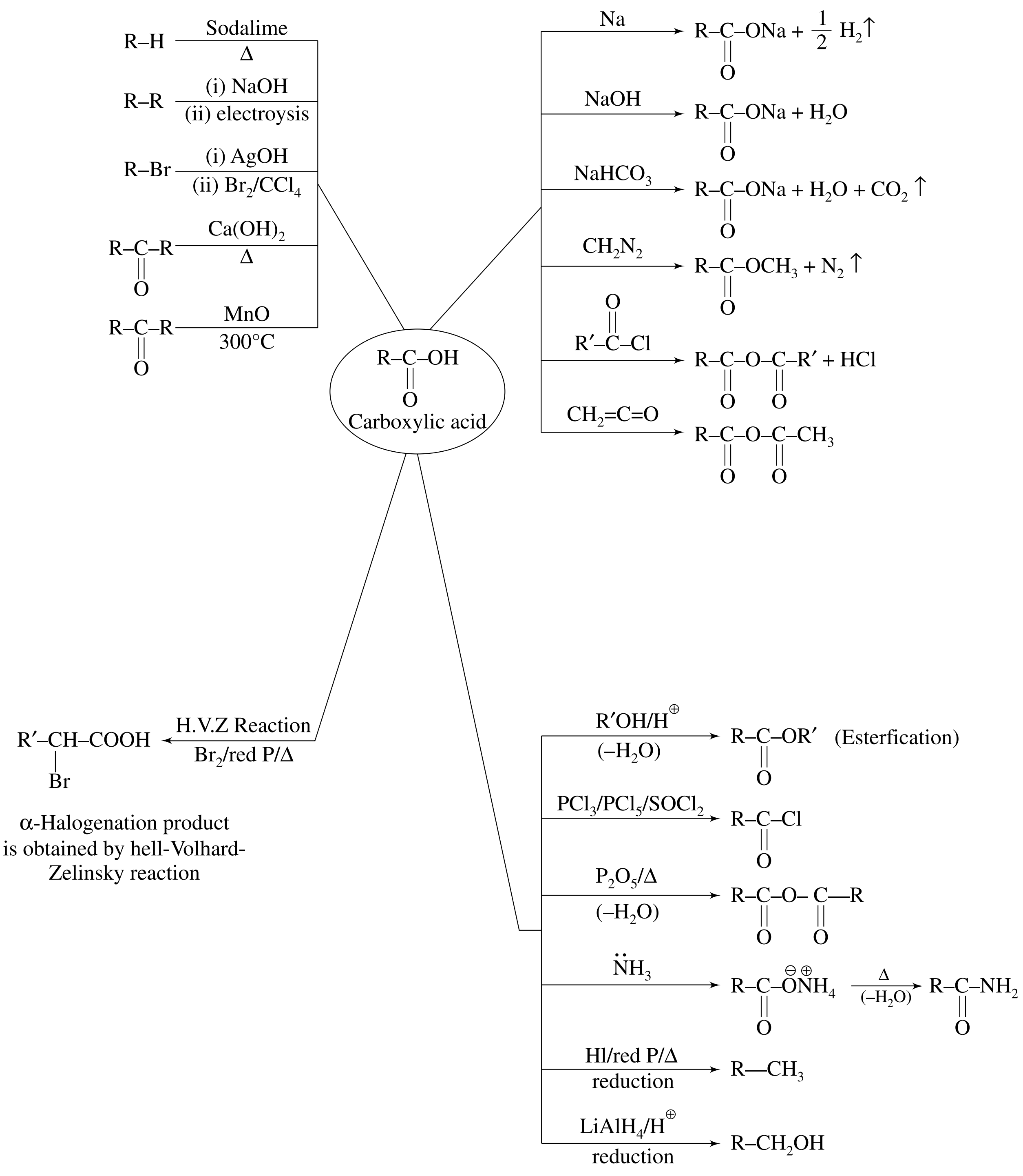


A dimer of a carboxylic acid

METHODS OF PREPARATION OF CARBOXYLIC ACIDS



CHEMICAL PROPERTIES OF CARBOXYLIC ACIDS



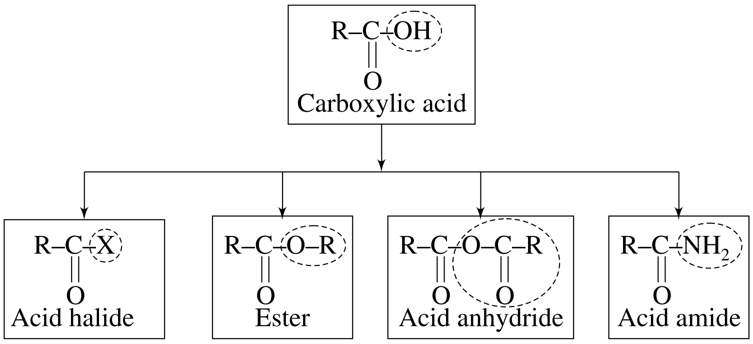
α-Halogenation product is obtained by hell-Volhard-Zelinsky reaction

COMPARISON OF FORMIC ACID AND ACETIC ACID

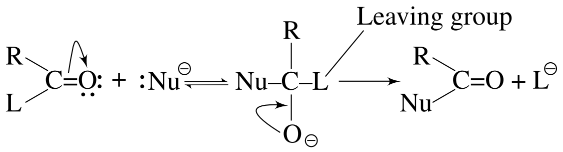
	Property	Formic acid	Acetic acid
1.	**Acidic nature**		
(i)	Reaction with electro positive metals	$HCOOH + Na \rightarrow HCOONa + 1/2\ H_2 \uparrow$	$CH_3COOH + Na \rightarrow CH_3COONa + 1/2\ H_2 \uparrow$
(ii)	Reaction with bases	$HCOOH + NaOH \rightarrow HCOONa + H_2O$	$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$
(iii)	Reaction with carbonates and bicarbonates	$HCOOH + NaHCO_3 \rightarrow HCOONa + H_2O + CO_2 \uparrow$	$CH_3COOH + NaHCO_3 \rightarrow$ $CH_3COONa + H_2O + CO_2 \uparrow$
2.	Esterification	$HCOOH + C_2H_5OH \rightarrow HCOOC_2H_5 + H_2O$	$CH_3COOH + C_2H_5OH$ $\xrightarrow[\text{Conc.}]{H_2SO_4} CH_3COOC_2H_5 + H_2O$
3.	Reaction with PCL_5	$HCOOH + PCl_5 \rightarrow HCOCl + POCl + HCl$ $\downarrow$ $CO + HCl$	$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$
4.	Heating Ammonium salts	$HCOONH_4 \rightarrow HCONH_2 + H_2O$	$CH_3COONH_4 \rightarrow CH_3CONH_2 + H_2O$
5.	Heating alone	$HCOOH \rightarrow CO_2 \uparrow + H_2 \uparrow$	Unaffected
6.	Reaction with conc. H_2SO_4	$HCOOH \xrightarrow[\text{Conc.}]{H_2SO_4} CO \uparrow + H_2O$	Unaffected
7.	Reaction with Cl_2/red P	Unaffected	Form $ClCH_2COOH$; $Cl_2CHCOOH$, Cl_3CCOOH
8.	Action of heat on salts		
(i)	Calcium salt	$(HCOO)_2Ca \rightarrow HCHO + CaCO_3$	$(CH_3COO)_2Ca \rightarrow CH_3COCH_3 + CaCO_3$
(ii)	Sodium salt	$2HCOONa \xrightarrow{360°C} \begin{array}{c} COONa \\ \mid \\ COONa \end{array} + H_2 \uparrow$	Unaffected
(iii)	Sodium salt (NaOH + CaO)	$HCOONa + NaOH \xrightarrow{CaO} Na_2CO_3 + H_2 \uparrow$	$CH_3COONa + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$
9.	Electrolysis of Na or K salt	$H_2 \uparrow$	$CH_3–CH_3$ formed
10.	On heating with P_2O_5	Unaffected	$2CH_3COOH \xrightarrow{P_2O_5} (CH_3CO)_2O + H_2O$
11.	Reducing nature		
(i)	Tollens' reagent	$HCOOH + Ag_2O \rightarrow 2Ag + CO_2 + H_2O$	Unaffected
(ii)	Fehling's solution	$HCOOH + 2CuO \rightarrow Cu_2O + CO_2 + H_2O$	Unaffected
(iii)	Mercuric chloride	$HCOOH + HgCl_2 \rightarrow Hg_2Cl_2 + CO_2 + 2HCl$ $HCOOH + Hg_2Cl_2 \rightarrow 2Hg + CO_2 + 2HCl$	Unaffected
12.	Acid (neutral solution) + $NaHSO_3$ + sodium Nitroprusside	Greenish blue colour	Unaffected
13.	Acid (neutral solution) + neutral ferric chloride	Red colour which changes to brown ppt. on heating.	Wine red colour
14.	Uses	(i) For preparation of CO_2 in laboratory. (ii) In the preservation of fruits. (iii) In the preparation of nickel formate, which is used as catalyst the hydrogenation of oil. (iv) As a reducing agent (v) In the manufacture of oxalic acid (vi) As an antiseptic and in the treatment of gout. (vii) As coagulating agent for rubber latex (viii) In lather tanning.	(i) As solvent and a laboratory reagent. (ii) For making various organic compound such as CH_3COCH_3; $(CH_3CO)_2O$; CH_3COCl, CH_3CONH_2 and CH_3COOR. (iii) For making various useful acetate, of Cu, Al, Fe, Cr, Pb. (a) $(CH_3COO)_2Cu$; Making green paints. (b) Al, Fe and Cr acetate; mordant in dying. (c) $(CH_3\ COO)_4$ Pb: oxidising agent. (iv) **Basic $(CH_3COO)_2Pb$:** manufacture of white lead. (v) Aluminium acetate; water proof fabrics. (vi) **Alkali acetate:** Diuretics (vii) **Cellulose acetate:** Artificial silk and Celluloid

CARBOXYLIC ACIDS DERIVATIVES

General Introduction



- Derivatives are characterised by **Nucleophilic Substitution Reaction** which take place at the acyl carbon (carbonyl group).



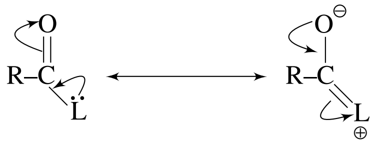
(L : Cl, OCOR', NH_2 or OR' or even –OH in acid)

- **Relative reactivity of acyl compounds:**

$$\text{R–}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{–Cl} > \text{R–}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{–O–}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{–R}' > \text{R–}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{–OR}' > \text{R–}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{–NH}_2$$

This overall order of reactivity can be accounted for in terms of the following three factors-

1. **Effects of the basicity on leaving group**
   - Weaker bases are good leaving group.
   - Hence acid derivative with weaker bases as leaving group are more reactive.
   - Chloride ion being the weakest base, acyl chloride is the most reactive of the acid derivatives.
   - Amines are the strongest bases (as compared to $Cl^{\ominus}$, $^{\ominus}OOCR$, $^{\ominus}OR$) hence are least reactive.
2. **Resonance effect**
   - The leaving group in each case has an atom with a lone pair of electron adjacent to carbonyl group.
   - The compound exists, therefore, as resonance hybrid



- The greater the stabilisation, the lower is the reactivity of the acyl compound.
- Acyl chlorides are the least affected by resonance due to the ineffective overlapping (i.e., 2p-orbital of carbon with 3p-orbital of Cl)
- Stabilisation is achieved by acid anhydride, ester and amide (due to effective overlapping of 2p-orbital of carbon–oxygen and carbon–nitrogen.)
- The stabilisation on particular carbon in acid anhydride is less than that of ester since the resonance effect is shared between two carbonyl groups.

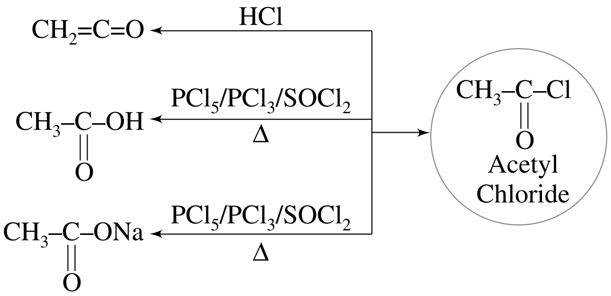
3. **Inductive effect**
   - The inductive effect of oxygen in ester is greater than that of nitrogen in amide. Hence ester is more reactive than an amide.

Special Points

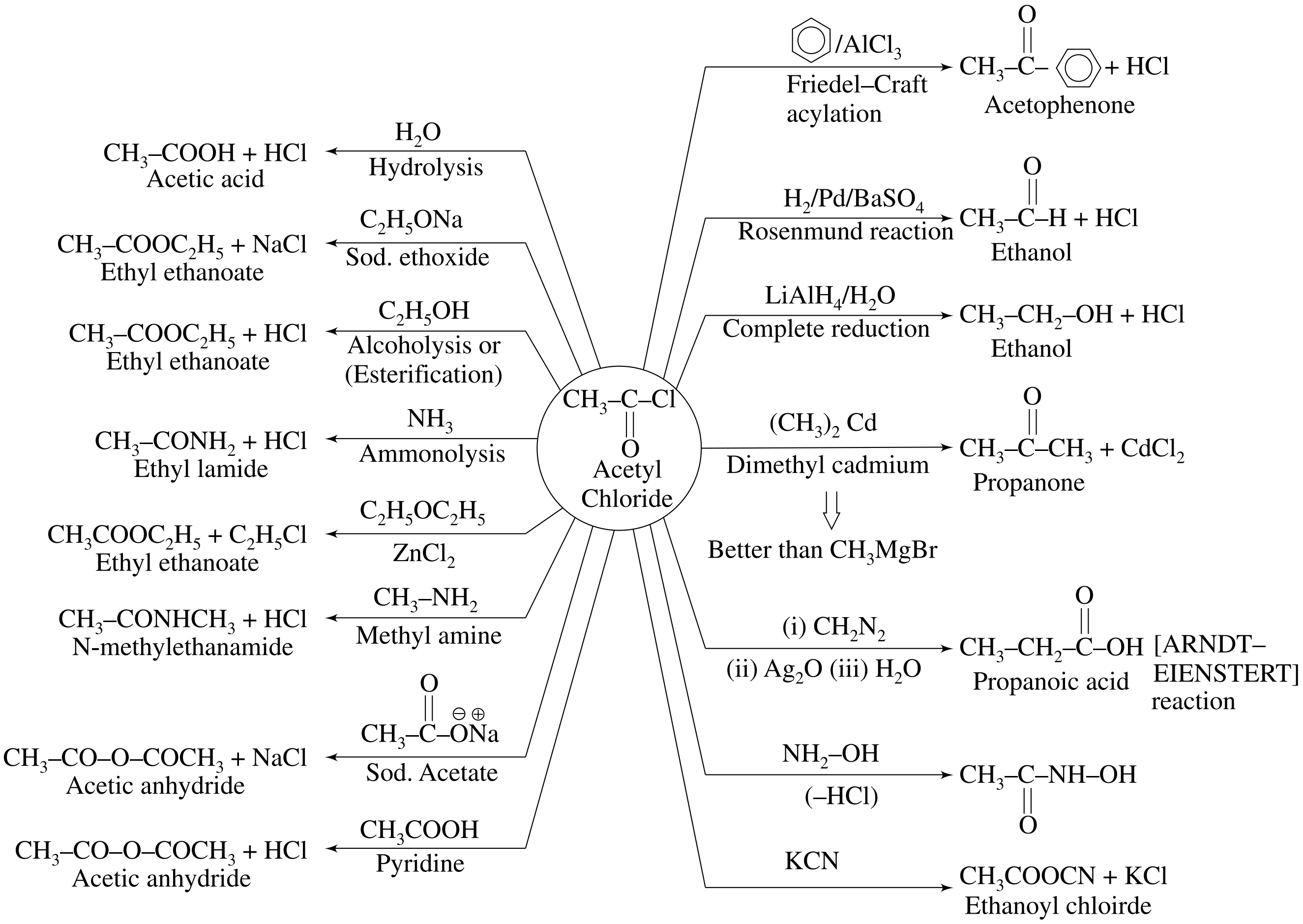
- Methyl acetate and ethyl acetate are Fruity smelling liquids.
- Acetamide is a white crystalline solid having pungent smell of dead mouse.

  Therefore, acid derivatatives have higher boiling points than corresponding hydrocarbons but lower boiling points than corresponding carboxylic acids.
- Primary amides have quite high boiling point and melting points because they form strong intermolecular H-bonding.

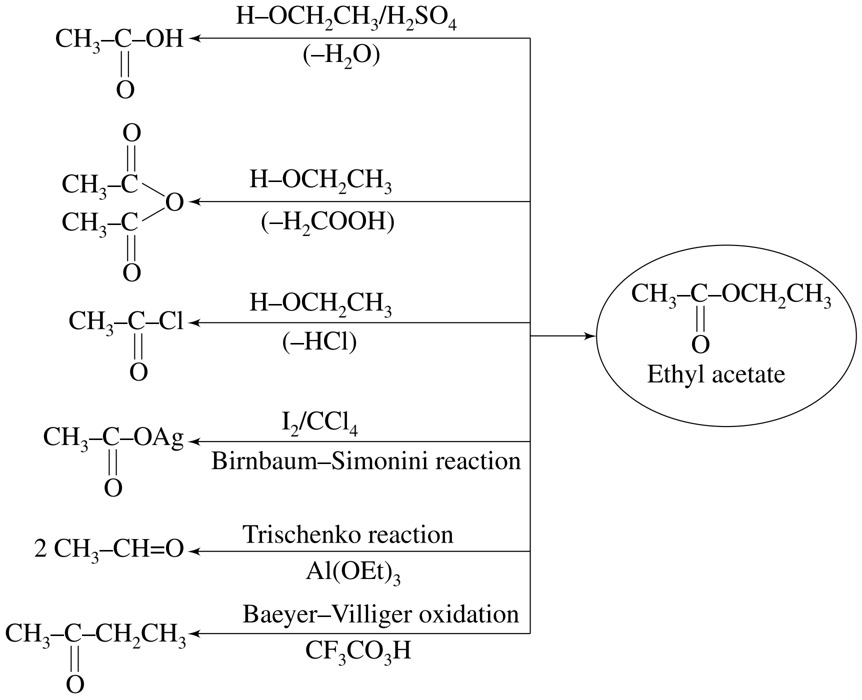
METHODS OF PREPARATION OF ACID CHLORIDE



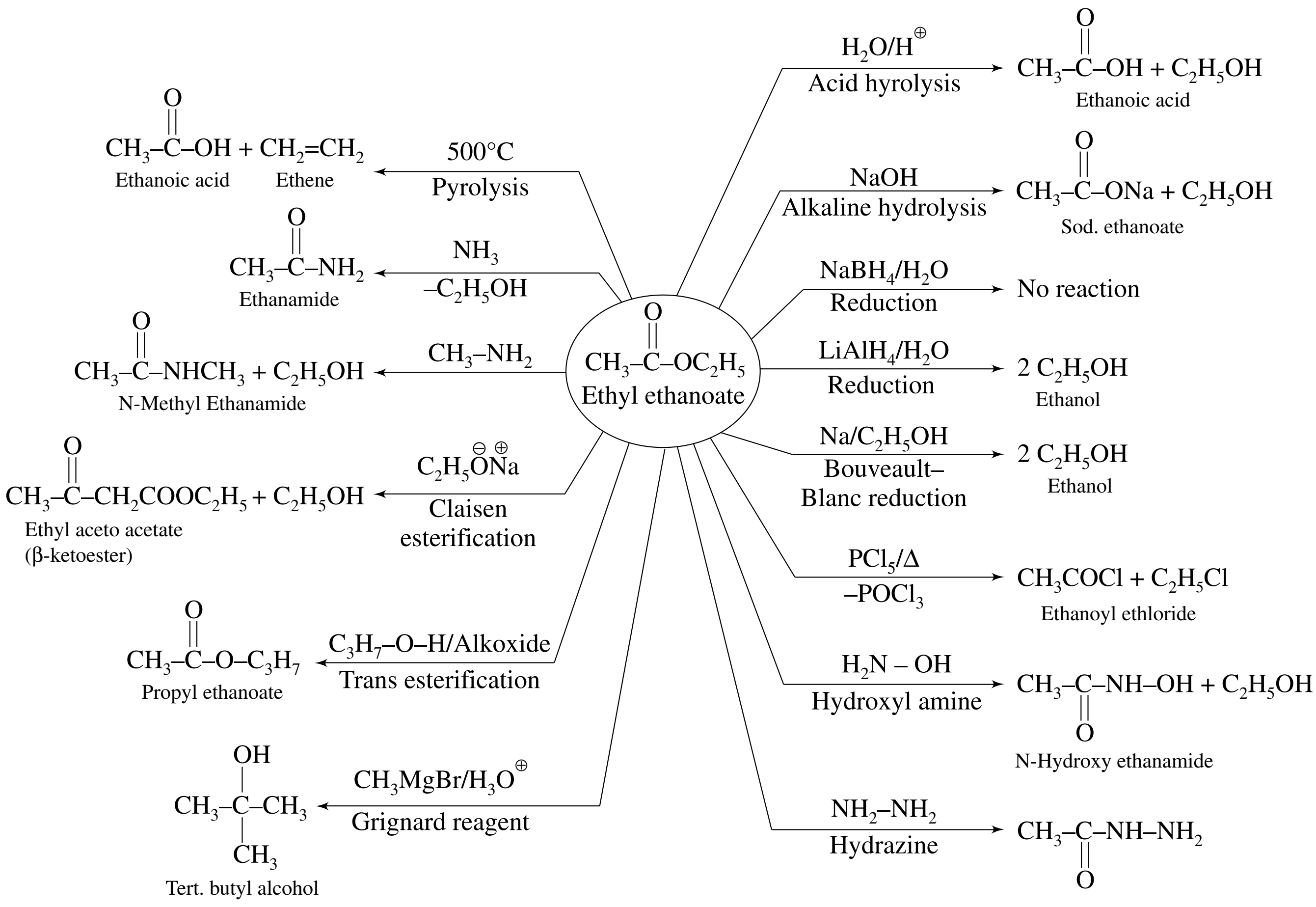
CHEMICAL PROPERTIES OF ACID CHILORIDE



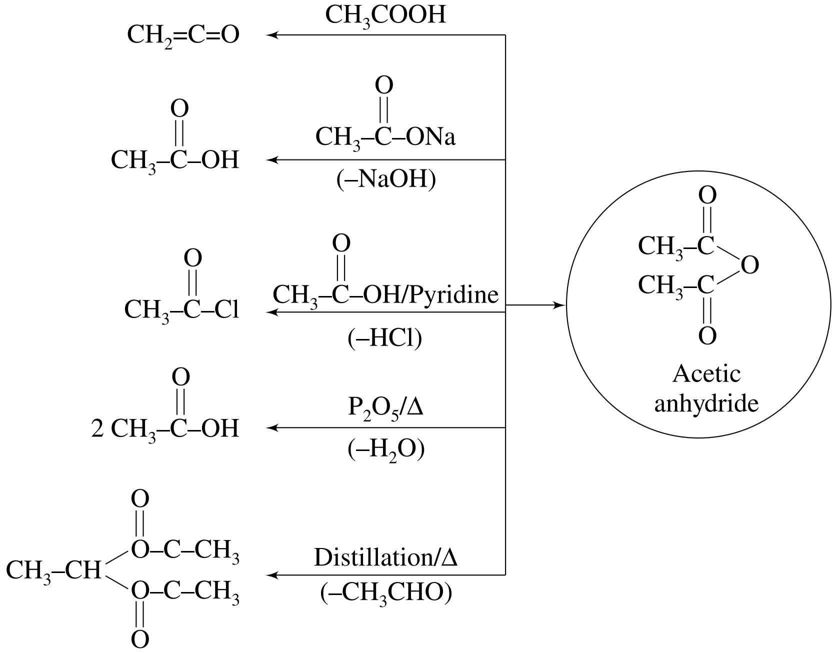
METHODS OF PREPARATION OF ESTER



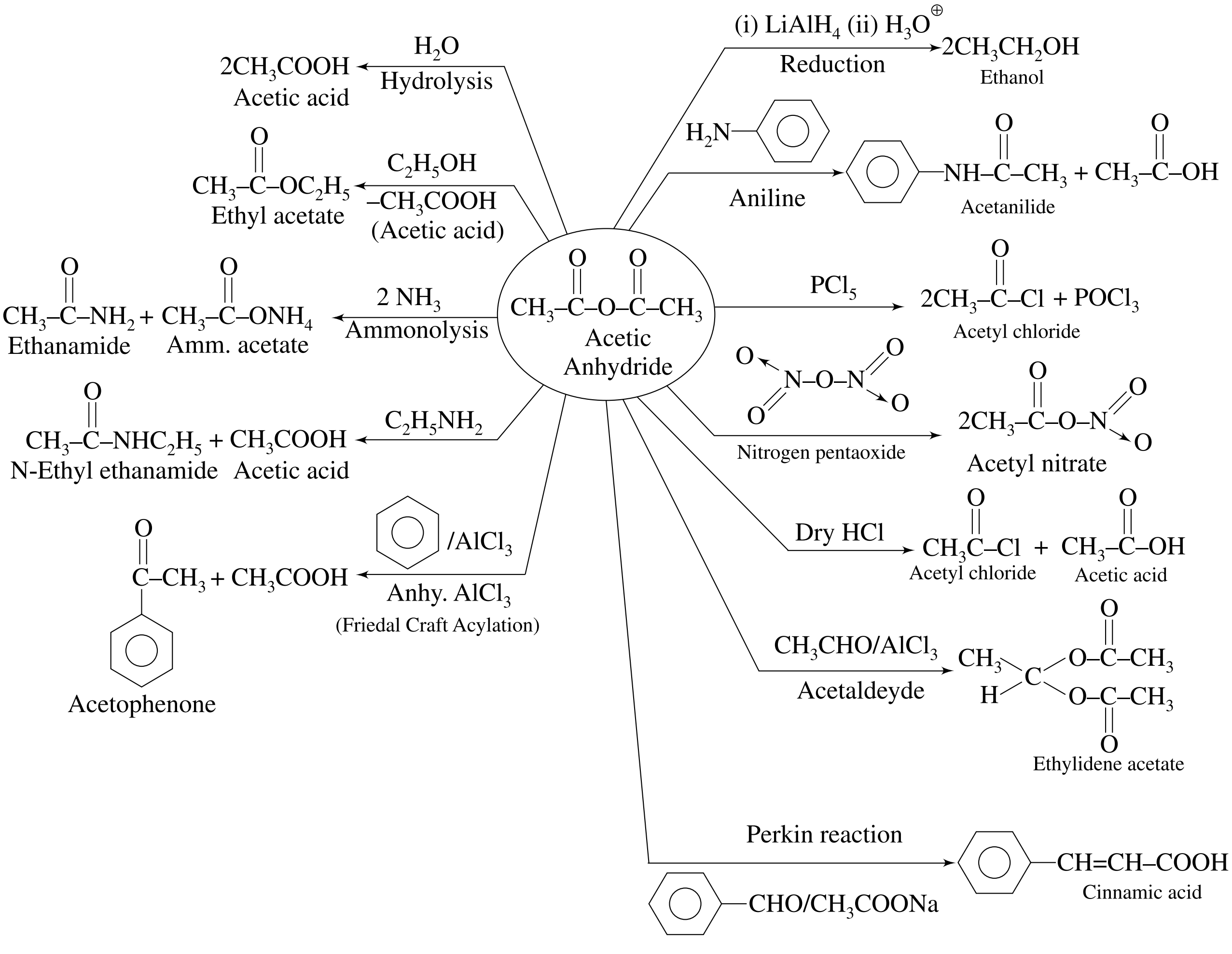
CHEMICAL PROPERTIES OF ESTER



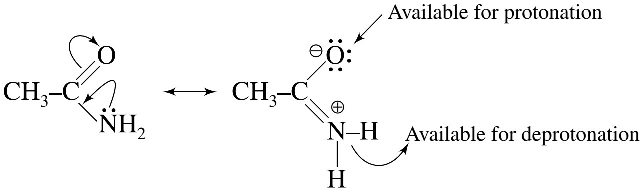
METHODS OF PREPARATION OF ACID ANHYDRIDE

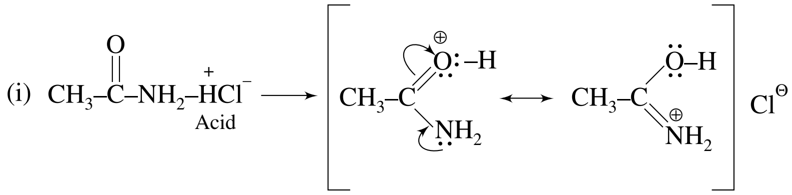


CHEMICAL PROPERTIES OF ACID ANHYDRIDE



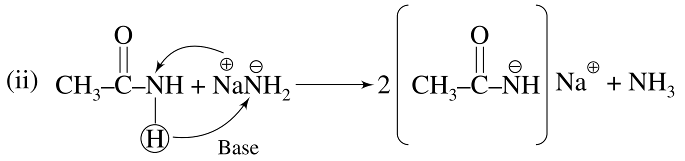
AMPHOTERIC CHARACTER OF ACETAMIDE:





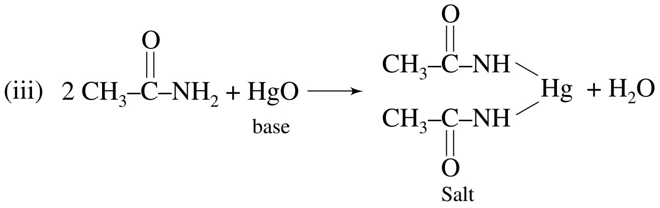
$$\text{(i)}\ CH_3\text{–}\overset{O}{\overset{\|}{C}}\text{–}\overset{+}{N}H_2\text{–}HCl^{-} \longrightarrow \left[CH_3\text{–}C(=\overset{\oplus}{O}\text{–}H)NH_2 \longleftrightarrow CH_3\text{–}C(\text{–}OH)=\overset{\oplus}{N}H_2\right] Cl^{\ominus}$$

Acid



$$\text{(ii)}\ CH_3\text{–}\overset{O}{\overset{\|}{C}}\text{–}NH + \overset{\oplus}{Na}\overset{\ominus}{N}H_2 \longrightarrow 2\left(CH_3\text{–}\overset{O}{\overset{\|}{C}}\text{–}\overset{\ominus}{N}H\right)Na^{\oplus} + NH_3$$

Base

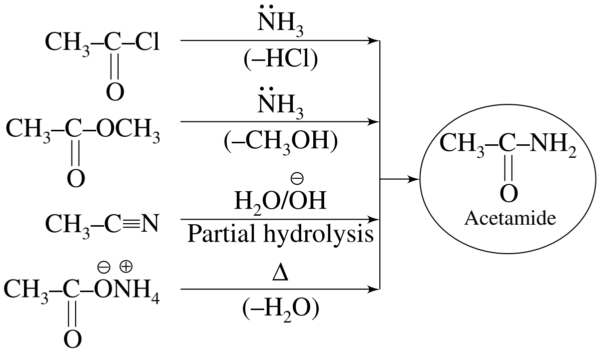


$$\text{(iii)}\ 2\,CH_3\text{–}\overset{O}{\overset{\|}{C}}\text{–}NH_2 + HgO \longrightarrow (CH_3\text{–}\overset{O}{\overset{\|}{C}}\text{–}NH)_2Hg + H_2O$$

base

Salt

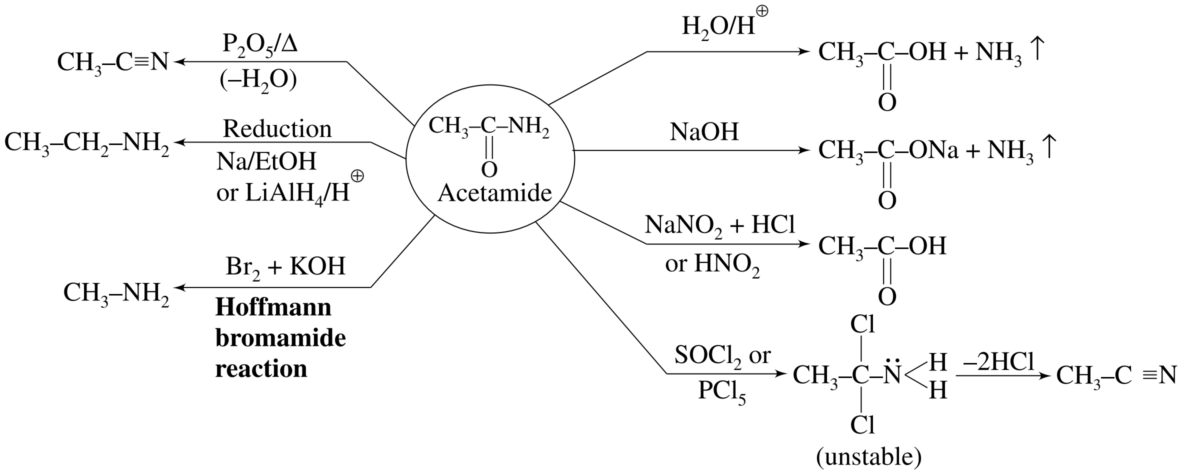
METHODS OF PREPARATION OF ACID AMIDE



$$CH_3\text{–}\underset{O}{\underset{\|}{C}}\text{–}Cl \xrightarrow[(-HCl)]{\ddot{N}H_3} \qquad CH_3\text{–}\underset{O}{\underset{\|}{C}}\text{–}OCH_3 \xrightarrow[(-CH_3OH)]{\ddot{N}H_3} \qquad CH_3\text{–}C\equiv N \xrightarrow[\text{Partial hydrolysis}]{H_2O/\overset{\ominus}{O}H} \qquad CH_3\text{–}\underset{O}{\underset{\|}{C}}\text{–}\overset{\ominus}{O}\overset{\oplus}{N}H_4 \xrightarrow[(-H_2O)]{\Delta} \quad CH_3\text{–}\underset{O}{\underset{\|}{C}}\text{–}NH_2$$

Acetamide

CHEMICAL PROPERTIES OF ACID AMIDE



$$CH_3\text{–}\underset{O}{\underset{\|}{C}}\text{–}NH_2 \text{ (Acetamide)} \xrightarrow[(-H_2O)]{P_2O_5/\Delta} CH_3\text{–}C\equiv N$$

$$\text{Acetamide} \xrightarrow[\text{Na/EtOH or } LiAlH_4/H^{\oplus}]{\text{Reduction}} CH_3\text{–}CH_2\text{–}NH_2$$

$$\text{Acetamide} \xrightarrow{Br_2 + KOH} CH_3\text{–}NH_2$$

Hoffmann bromamide reaction

$$\text{Acetamide} \xrightarrow{H_2O/H^{\oplus}} CH_3\text{–}\underset{O}{\underset{\|}{C}}\text{–}OH + NH_3\uparrow$$

$$\text{Acetamide} \xrightarrow{NaOH} CH_3\text{–}\underset{O}{\underset{\|}{C}}\text{–}ONa + NH_3\uparrow$$

$$\text{Acetamide} \xrightarrow[\text{or } HNO_2]{NaNO_2 + HCl} CH_3\text{–}\underset{O}{\underset{\|}{C}}\text{–}OH$$

$$\text{Acetamide} \xrightarrow[PCl_5]{SOCl_2 \text{ or}} CH_3\text{–}\overset{Cl}{\underset{Cl}{C}}\text{–}\ddot{N}H_2 \xrightarrow{-2HCl} CH_3\text{–}C\equiv N$$

(unstable)

SOLVED EXAMPLE

1. Pyruvic acid is obtained by

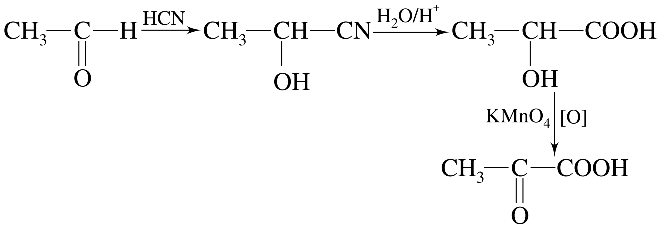
(1) Acidic hydrolysis of acetone cyanohydrin

(2) Acidic hydrolysis of acetaldehyde cyanohydrin followed by acidification with $KMnO_4$

(3) Acidic hydrolysis of formaldehyde cyanohydrin

(4) Reaction of HCN with CH_3CHO followed by treatment with $NaOH/I_2$

Sol. **[2]**



$$CH_3-\underset{\underset{O}{\|}}{C}-H \xrightarrow{HCN} CH_3-\underset{\underset{OH}{|}}{CH}-CN \xrightarrow{H_2O/H^+} CH_3-\underset{\underset{OH}{|}}{CH}-COOH$$

$$\Big\downarrow KMnO_4\ [O]$$

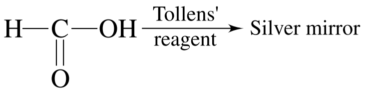
$$CH_3-\underset{\underset{O}{\|}}{C}-COOH$$

2. Formic acid and acetic acid are distinguished by

(1) $NaHCO_3$ (2) $FeCl_3$

(3) Victor Meyer's test (4) Tollens' reagent

Sol. **[4]**



$$H-\underset{\underset{O}{\|}}{C}-OH \xrightarrow[\text{reagent}]{\text{Tollens'}} \text{Silver mirror}$$

Formic acid (Aldehyde group)

$$CH_3COOH \xrightarrow[\text{reagent}]{\text{Tollens'}} \text{Negative test}$$

Absence of aldehyde group

3. An organic liquid of the composition $C_4H_8O_2$ yields a sodium salt of an acid $C_3H_6O_2$ and methanol on boiling with NaOH solution. The given liquid is

(1) $CH_3CH_2COOCH_3$ (2) $CH_3COOC_2H_5$

(3) $HCOOC_3H_7$ (4) $CH_3CH_2CH_2COOH$

Sol. **[1]**

$$CH_3-CH_2-CO|O-CH_3 \xrightarrow{NaOH} CH_3-CH_2-COONa+|CH_3OH$$

4. When propionic acid is treated with aqueous sodium bicarbonate, CO_2 is liberated. The C of CO_2 comes from:

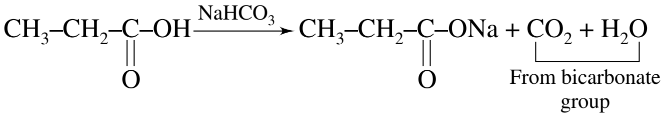
(1) methyl group

(2) carboxylic acid group

(3) methylene group

(4) bicarbonate group

Sol. **[4]**



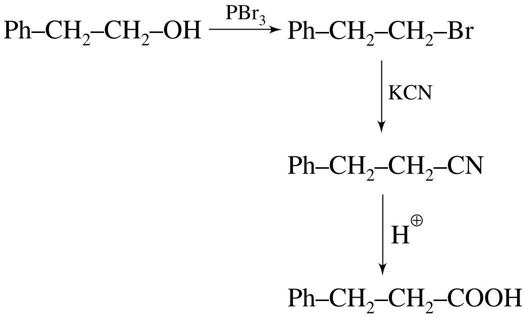
$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{NaHCO_3} CH_3-CH_2-\underset{\underset{O}{\|}}{C}-ONa + \underbrace{CO_2 + H_2O}_{\text{From bicarbonate group}}$$

5. $Ph-CH_2-CH_2OH$ can be converted into $PhCH_2CH_2COOH$. The correct sequence of reagents is

(1) PBr_3, KCN, H^+ (2) PBr_3, KCN, H_2

(3) KCN, H^+, PBr_3 (4) PBr_3, HCN, H^+

Sol. **[1]**



$$Ph-CH_2-CH_2-OH \xrightarrow{PBr_3} Ph-CH_2-CH_2-Br$$

$$\Big\downarrow KCN$$

$$Ph-CH_2-CH_2-CN$$

$$\Big\downarrow H^{\oplus}$$

$$Ph-CH_2-CH_2-COOH$$

6. When benzyl chloride is treated with ethanolic KCN, followed by acidification, the major product formed is:

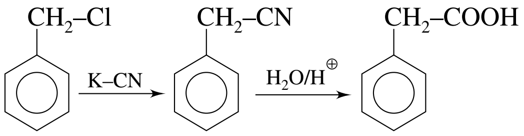
(1) benzoic acid

(2) benzyl alcohol

(3) benzyl cyanide

(4) phenyl acetic acid

Sol. **[4]**



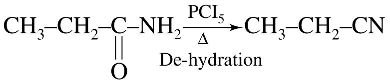
Phenyl acetic acid

7. Guess the product $CH_2CH_2CONH_2 \xrightarrow[\Delta]{PCI_5} ?$

(1) CH_3CH_2-CN (2) CH_3CH_2COCI

(3) $CH_3CCl_2CONH_2$ (4) $CH_3CH_2CCl_2-NH_2$

Sol. **[1]**



$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow[\Delta]{PCl_5} CH_3-CH_2-CN$$

De-hydration

8. Which of the following reagents can distinguish 4-oxopentanoic acid from 2-oxopentanoic acid?

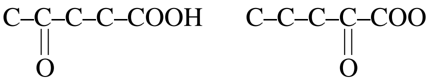
(1) $NaHCO_3$

(2) 2,4-Dinitrophenylhydrazine

(3) $AgNO_3$, aq. NH_3

(4) I_2,NaOH

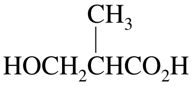
Sol. **[4]**

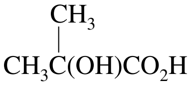


$$C-\underset{\underset{O}{\|}}{C}-C-C-COOH \qquad C-C-C-\underset{\underset{O}{\|}}{C}-COOH$$

$NaHCO_3$	+Ve	+Ve
DNP	+Ve	+Ve
$AgNO_3$/aq NH_3	–Ve	–Ve
I_2/NaOH	+Ve	–Ve

9. A compound (X), $C_4H_8O_3$, liberates CO_2 on reaction with $NaHCO_3$. When (X) is treated with pyridinium chlorochromate, it is converted into a new compound (Y), $C_4H_6O_3$, which on heating expels CO_2 to form acetone. The compound (X) is:

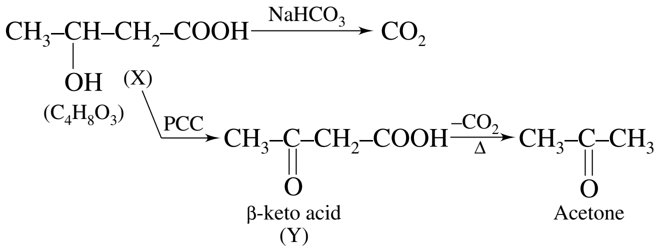
(1) 
$HOCH_2\overset{CH_3}{\overset{|}{C}}HCO_2H$

(2) 
$CH_3\overset{CH_3}{\overset{|}{C}}(OH)CO_2H$

(3) $CH_3CHOHCH_2CO_2H$

(4) $CH_3CH_2CH(OH)CO_2H$

Sol. **[3]**



10. Carboxylic acids, RCOOH, furnish H^+ ions to water forming H_3O^+ and carboxylate ions, $RCOO^-$. The major reason for this acidic behaviour is that

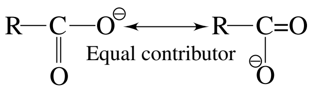
(1) The carboxylate ion is stabilised by salvation with H_2O

(2) The carboxylic acid is stabilised by resonance

(3) The carboxylate ion is stabilised by resonance

(4) The carboxylate ion is more resonance stabilised than the unionised carboxylic acid is

Sol. **[4]**

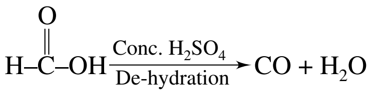


11. Formic acid on being heated with concentrated H_2SO_4 is converted into:

(1) CH_3COOH (2) CO

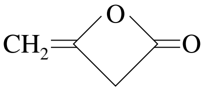
(3) CO_2 (4) HOOCCOOH

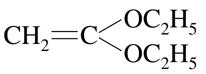
Sol. **[2]**


$$H\text{–}\overset{O}{\overset{\|}{C}}\text{–}OH \xrightarrow[\text{De-hydration}]{\text{Conc. } H_2SO_4} CO + H_2O$$

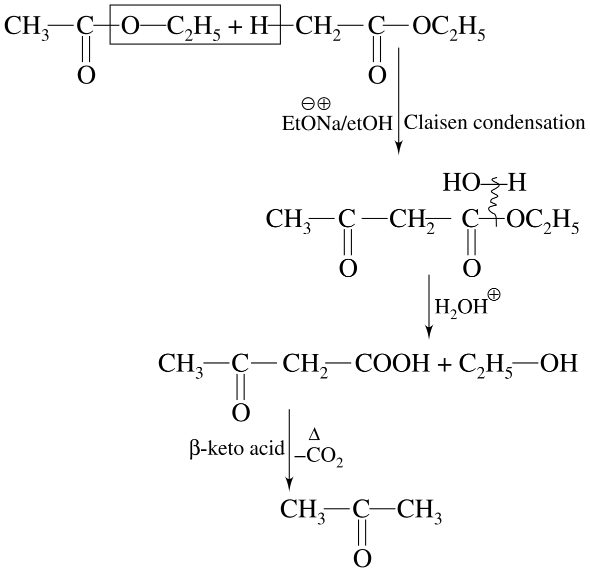
12. $CH_3CO_2C_2H_5$ on reaction with sodium ethoxide in ethanol gives A, which on heating in the presence of acid gives B compound B is-

(1) CH_3COCH_2COOH (2) CH_3COCH_3

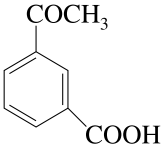
(3) 

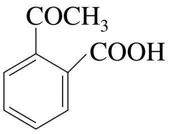
(4) 

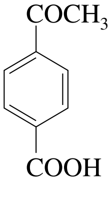
Sol. **[2]**

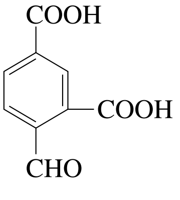


13. An aromatic compound 'X' ($C_9H_8O_3$) turns blue litmus to red. It gives yellow precipitate with I_2/NaOH and forms Y($C_8H_6O_4$). Y forms three mononitro isomeric products. Identify X.

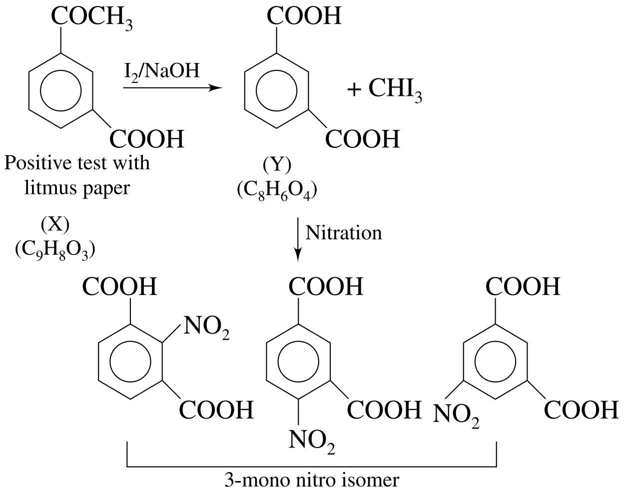
(1) 

(2) 

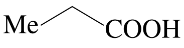
(3) 

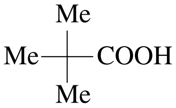
(4) 

Sol. **[1]**



14. The following acids can be differentiated by

(I) 

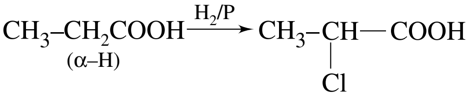
(II) 

(1) $NaHCO_3$ (2) $AgNO_3$

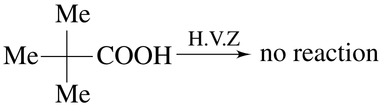
(3) H. V. Z. reaction (4) Hunsdiecker reaction

Sol. **[3]**

(I) Only α–H containing carboxylic acid forms-halo acid with X_2/P_4 is known as H. V. Z reaction



$$\underset{(\alpha\text{–H})}{CH_3\text{–}CH_2COOH} \xrightarrow{H_2/P} CH_3\text{–}\underset{\substack{|\\ Cl}}{CH}\text{—}COOH$$

(II) 

$$Me\text{–}\overset{Me}{\underset{Me}{C}}\text{–}COOH \xrightarrow{H.V.Z} \text{no reaction}$$

15. Formic acid is obtained when:

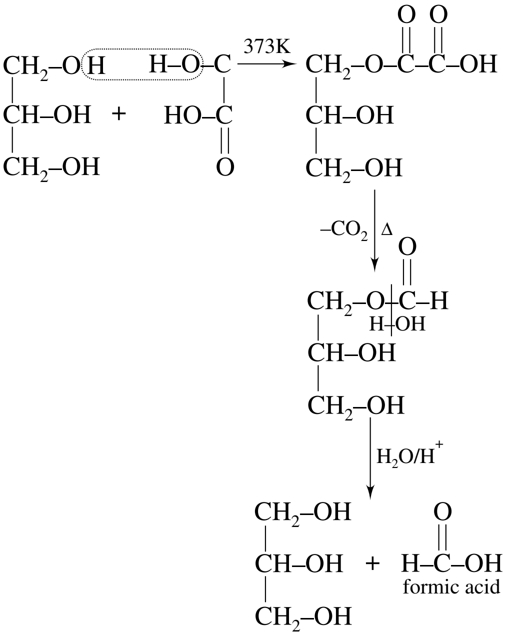
(1) Calcium acetate is heated with conc. H_2SO_4

(2) Calcium formate is heated with calcium acetate

(3) Glycerol is heated with oxalic acid at 373 K

(4) Acetaldehyde is oxidised with $K_2Cr_2O_7$ and H_2SO_4

Sol. **[3]**



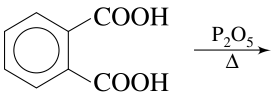
EXERCISE 1

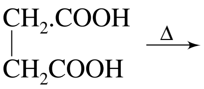
1. Which reactions give acid anhydride as product?

(i) $C_6H_5COOH + CH_3COCl \xrightarrow{\text{Pyridine}}$

(ii) $C_6H_5COO^{\ominus}Na^{\oplus} + C_6H_5COCl \longrightarrow$

(iii) $C_6H_5CONH_2 + CH_3COO^{\ominus}\ Na^{\oplus} \longrightarrow$

(iv) 

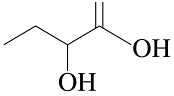
(v) 

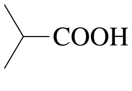
$$\begin{array}{l} CH_2.COOH \\ | \\ CH_2COOH \end{array} \xrightarrow{\Delta}$$

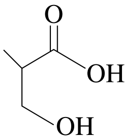
(1) i, ii, iii, iv only (2) i, ii, iv, v only

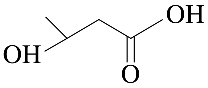
(3) i, ii, iii only (4) iv & v only

2. An optically active compound 'X' has molecular formula $C_4H_8O_3$. It evolves CO_2 with $NaHCO_3$. 'X' on reaction with $LiAlH_4$ give achiral compound. 'X' is–

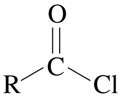
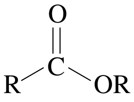
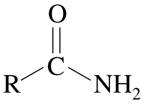
(1) 

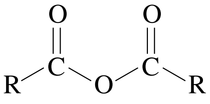
(2) 

(3) 

(4) 

3. The order of decreasing ease of hydrolysis of the compound

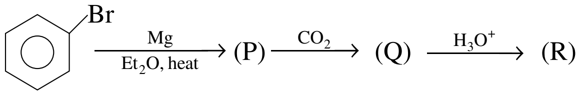
   and

 is

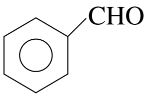
(1) I > IV > II > III (2) I > II > III > IV

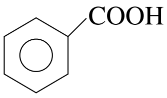
(3) I > III > II > IV (4) IV > III > II > I

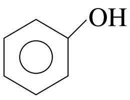
4. Consider the following sequence of reaction.

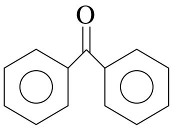


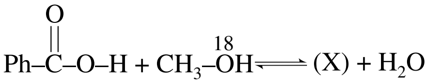
The final product (R) is

(1) 

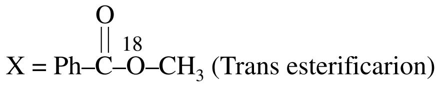
(2) 

(3) 

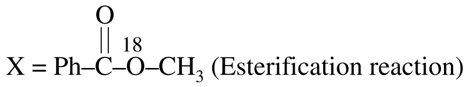
(4) 

5. 

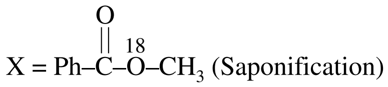
$Ph\text{–}\overset{\overset{O}{\|}}{C}\text{–}O\text{–}H + CH_3\text{–}\overset{18}{O}H \rightleftharpoons (X) + H_2O$

(1) 

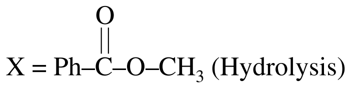
$X = Ph\text{–}\overset{\overset{O}{\|}}{C}\text{–}\overset{18}{O}\text{–}CH_3$ (Trans esterificarion)

(2) 

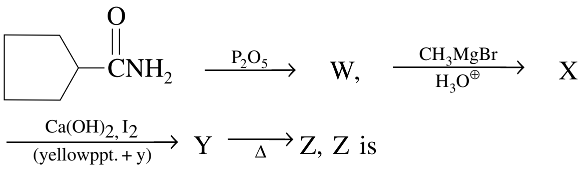
$X = Ph\text{–}\overset{\overset{O}{\|}}{C}\text{–}\overset{18}{O}\text{–}CH_3$ (Esterification reaction)

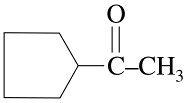
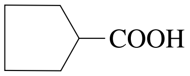
(3) 

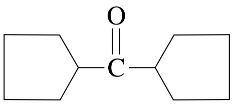
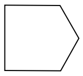
$X = Ph\text{–}\overset{\overset{O}{\|}}{C}\text{–}\overset{18}{O}\text{–}CH_3$ (Saponification)

(4) 

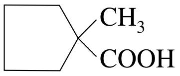
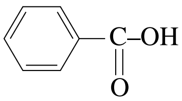
$X = Ph\text{–}\overset{\overset{O}{\|}}{C}\text{–}O\text{–}CH_3$ (Hydrolysis)

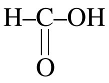
6. 

(1) 
(2) 

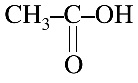
(3) 
(4) 

7. Which of the following give HVZ reaction?

(1) 
(2) 

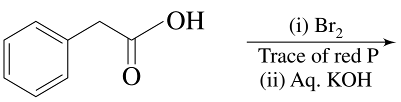
(3) 

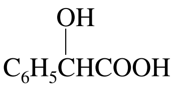
$H\text{–}\underset{\underset{O}{\|}}{C}\text{–}OH$

(4) 

$CH_3\text{–}\underset{\underset{O}{\|}}{C}\text{–}OH$

8. Give the major product of the following reaction sequence:



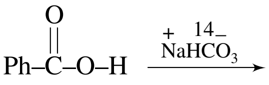
(1) 

$C_6H_5\overset{\overset{OH}{|}}{C}HCOOH$

(2) $C_6H_5CH_2COBr$

(3) *p*-Br-$C_6H_4CH_2COOH$

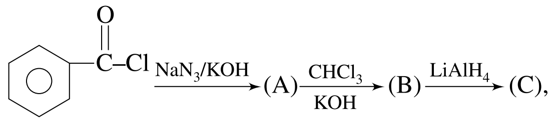
(4) *m*-Br-$C_6H_4CH_2COOH$

9. 

$Ph\text{–}\overset{\overset{O}{\|}}{C}\text{–}O\text{–}H \xrightarrow{+\ \overset{14}{N}aHC\overset{-}{O}_3}$ the gas evolved is:

(1) CO_2 (2) $\overset{14}{C}O_2$

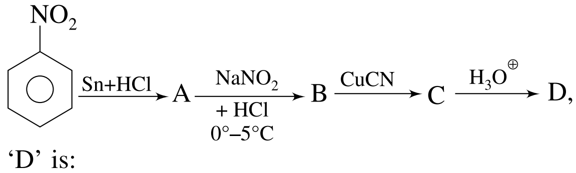
(3) H_2 (4) NH_3

10. 

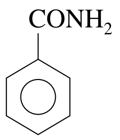
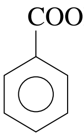
Identify C

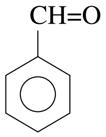
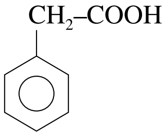
(1) $Ph\text{–}CH_2\text{–}NH_2$ (2) $Ph\text{–}NH_2$

(3) $Ph\text{–}CO_2H$ (4) $Ph\text{–}NH\text{–}CH_3$

11. 

'D' is:

(1) 
(2) 

(3) 
(4) 

12. The conversion $CH_3OH \to CH_3COOH$ can be effected by allowing CH_3OH to react with

(1) carbon monoxide in the presence of Monsanto catalyst, a complex compound of rhodium, $[Rh(CO)_2I_2]^-$

(2) formic acid in the presence of concentrated H_2SO_4

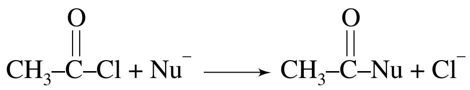
(3) ethylene in the presence of $PdCl_2$

(4) formaldehyde in the presence of dry HCl gas

13. In a nucleophilic acyl substitution, the hybridisation of carbon atom at the substrate centre changes in the order (substrate → intermediate → product)

(1) $sp^2 \to sp^2 \to sp^2$ (2) $sp^3 \to sp^3 \to sp^2$

(3) $sp^2 \to sp^3 \to sp^2$ (4) $sp^2 \to sp^2 \to sp^3$

14. 

$CH_3\text{–}\overset{\overset{O}{\|}}{C}\text{–}Cl + Nu^- \longrightarrow CH_3\text{–}\overset{\overset{O}{\|}}{C}\text{–}Nu + Cl^-$

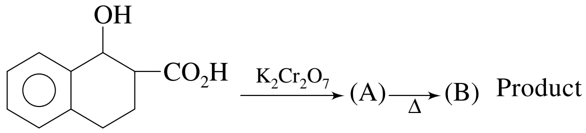
The reactivity order of different nucleophiles (NH_2^-, CH_3COO^-, HO^-) is in order

(1) $NH_2^- < CH_3COO^- < OH^-$

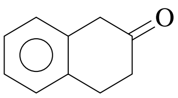
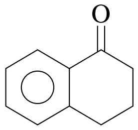
(2) $CH_3COO^- < OH^- < NH_2^-$

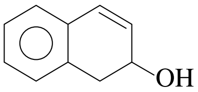
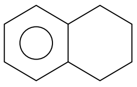
(3) $NH_2^- < OH^- < CH_3COO^-$

(4) $CH_3COO^- < NH_2^- < OH^-$

15. 

(B) is:

(1)  (2) 

(3)  (4) 

16. The conversion of acetophenone into benzoic acid can be achieved by reaction with:

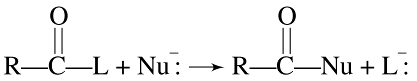
(1) sodium hydroxide followed by acidification

(2) iodine and sodium hydroxide, followed by acidification

(3) hydroxylamine followed by reaction with H_2SO_4

(4) *m*-chloroperoxobenzoic acid

17. The nucleophilic acyl substitution



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-L + Nu\bar{:} \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-Nu + L\bar{:}$$

will occur smoothly if:

(1) $Nu:^-$ is a stronger base than $L:^-$

(2) $Nu:^-$ is a weaker base than $L:^-$

(3) $Nu:^-$ and $L:^-$ have equal basicity

(4) $R:^-$, $Nu:^-$ and $L:^-$ all have equal basicity

18. Consider the following sequence of reactions,

$PCl_5 + SO_2 \rightarrow A + B$

$CH_3COOH + A \rightarrow C + SO_2 + HCl$

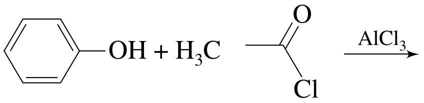
$2C + (CH_3)_2Cd \rightarrow 2D + CdCl_2$

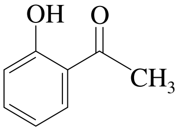
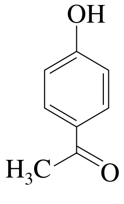
The end product (D) is:

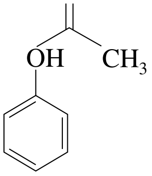
(1) CH_3COCl (2) CH_3COOCH_3

(3) CH_3COCH_3 (4) $(CH_3)_2CHCOCl$

19. Predict the product of the reaction below:



(1)  (2) 

(3)  (4) Both (1) and (2)

20. Which of the following does not give benzoic acid on hydrolysis?

(1) phenyl cyanide (2) benzoyl chloride

(3) benzyl chloride (4) methyl benzoate

21. $CH_3CH_2ONa \xrightarrow[\text{Pressure (ii) } H^+]{\text{(i) CO, } \Delta} A$

$CH_2 = CH_2 + CO + H_2O \xrightarrow[670°C]{H_3PO_4} B$

A and B are:

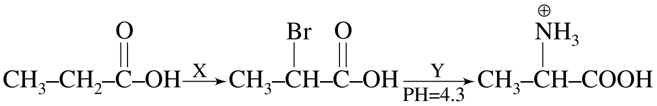
(1) CH_3CH_2COOH in both cases

(2) CH_3CH_2CHO in both cases

(3) CH_3CH_2COOH, CH_3CHO

(4) CH_3CHO, CH_3COOH

22. Which of the following sets of reagents X and Y will convert propanoic acid into alanine (an amino acid)?



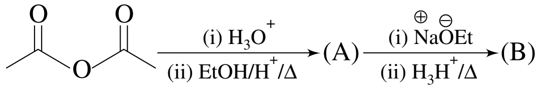
$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow{X} CH_3-\overset{\overset{\displaystyle Br}{|}}{CH}-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow[PH=4.3]{Y} CH_3-\overset{\overset{\displaystyle \overset{\oplus}{N}H_3}{|}}{CH}-COOH$$

	X	Y
(1)	Br_2	$NaNH_2$
(2)	Br_2/P	NaOH
(3)	Br_2/P	NH_3
(4)	Br_2/HBr	$NaNH_2$

23. Which of the following compounds will develop a blue colour on successive treatment with aqueous KI containing KIO_3 and starch solution?

(1) Benzoic acid (2) Phenol

(3) Ethanol (4) Ethyl acetate

24. 

Select correct option

(1) Compound (B) is acetone

(2) Compound (B) is acetic acid

(3) Compound (B) is ethyl acetate

(4) Compound (A) evolve H_2 (g) on reacting with Na-metal

25. Ethyl acetate is hydrolysed by heating with an aqueous NaOH solution. Which one of the following is the correct mechanism of the reaction?

(1) Acyl-oxygen bond cleavage; unimolecular

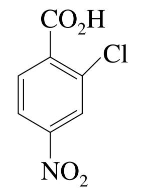
(2) Acyl-oxygen bond cleavage; bimolecular

(3) Alkyl-oxygen bond cleavage; unimolecular

(4) Alkyl-oxygen bond cleavage; bimolecular

EXERCISE 2

1. Which one of the following is the best synthesis of 2-chloro-4-nitrobenzoic acid?



2-chloro-4-nitrobenzoic

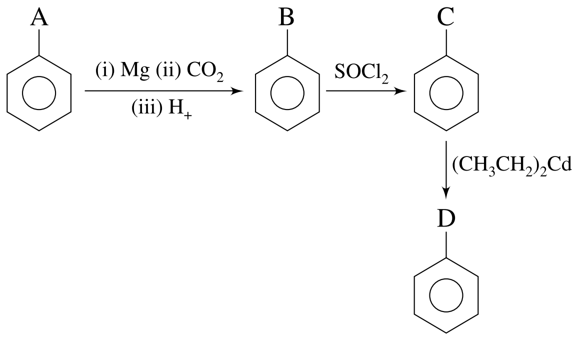
(1) 1. Heat benzoic acid with HNO_3, H_2SO_4
    2. Cl_2, $FeCl_3$, heat

(2) 1. Treat toluene with HNO_3, H_2SO_4
    2. $K_2Cr_2O_7$, H_2O, H_2SO_4, heat
    3. Cl_2, $FeCl_3$, heat

(3) 1. Treat toluene with HNO_3, H_2SO_4
    2. Cl_2, $FeCl_3$, heat
    3. $K_2Cr_2O_7$, H_2O, H_2SO_4, heat

(4) 1. Treat nitrobenzene with Cl_2, $FeCl_3$, and heat
    2. CH_3Cl, $AlCl_3$
    3. $K_2Cr_2O_7$, H_2O, H_2SO_4, heat

2. Consider the following sequence of reactions:



Identify A, B, C and D

	A	B	C	D
(1)	–F,	–$COCH_3$,	–COC_3H_7	–CHO
(2)	–CHO,	–COOH,	–COCl,	–COC_2H_5
(3)	–Br,	–COOH,	–COCl,	–COC_2H_5
(4)	–Br,	–COOH,	–COCl,	–CHO

3. The products A, B, C and D in the reaction

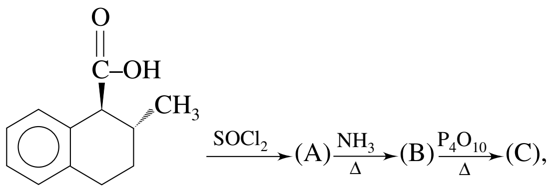
$$A + B \xleftarrow[H_2SO_4]{\text{Heat}} H\text{–}COOH \xrightarrow[H_2SO_4]{\text{Conc.}} C + D$$

are given by the set:

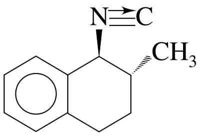
(1) CO, H_2O, CO_2, H_2 (2) CH_2, H_2O, CO, H_2

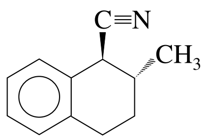
(3) CO_2, H_2, CO, H_2O (4) CO, H_2, CO_2, H_2O

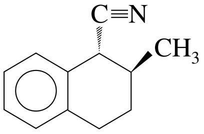
4.

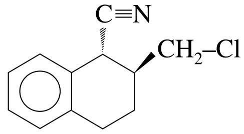


structure of (C) is–

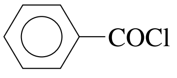
(1)


(2)


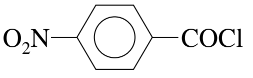
(3)


(4)


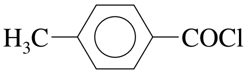
5. Consider the following compounds.



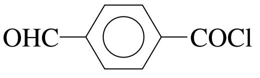
I



II



III



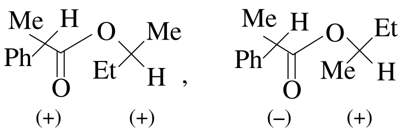
IV

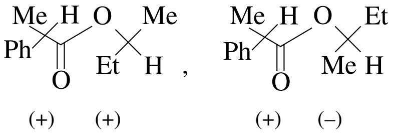
The correct order of decreasing reactivity of the above compounds towards hydrolysis is

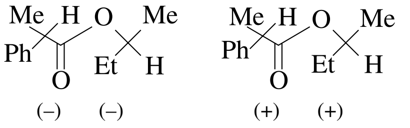
(1) II > IV > III > I (2) II > IV > I > III

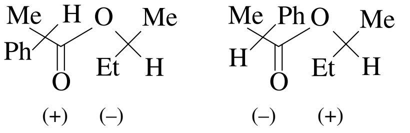
(3) I > II > III > IV (4) IV > II > I >III

6. A racemic mixture of (±) 2-phenyl propanoic acid on esterification with (+) 2-butanol gives two esters. Mention the stereochemistry of two esters formed.

(1)


(2)


(3)


(4)


7. Consider the following sequence of reactions:

$BaCO_3 + H_2SO_4 \rightarrow X(gas)$

$$CH_2 = CHBr \xrightarrow[\substack{2.\ X \\ 3.\ H_3O^+}]{1.\ Mg,\ THF,\ heat}$$

The product (Y) is:

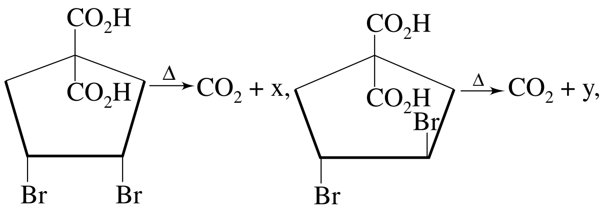
(1) $CH_2 = CHCHO$

(2) $CH_2{=}CHCOOH$

(3) $CH_2{=}CHCOBr$

(4) $CH_3CH{=}CHCH_2CH_2NH_2$

8. Products obtained in the given reaction are shown below:



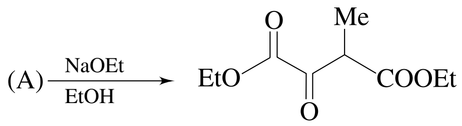
(*cis*) (*trans*)

The number of possible products for x and y is:

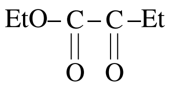
(1) 1, 1 (2) 1, 2

(3) 2, 1 (4) 2, 2

9. The reactant (A) is the reaction is:



(1) MeCOOEt and



$EtO{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}Et$

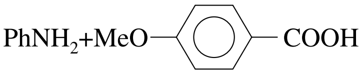
(2) EtCOOEt + EtOOC – COOEt

(3)

$EtOOC{-}\underset{\underset{Me}{|}}{CH}{-}COOEt + HCOOEt$

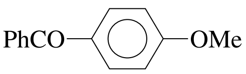
(4) EtCOOEt + HCOOEt

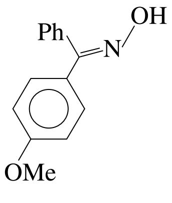
10. Ketone (A) $\xrightarrow{NH_2OH.HCl}$ (B) $\xrightarrow{H^{\oplus}}$

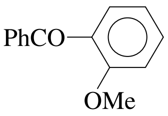


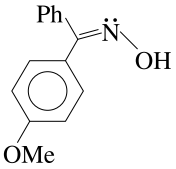
The ketone (A) and compound (B), respectively, are:

Ketone (A) **Compound (B)**

(I) 

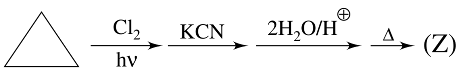
(III) 

(II) 

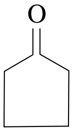
(IV) 

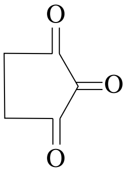
(1) (I), (III) (2) (I), (IV)

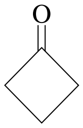
(3) (II), (III) (4) (II), (IV)

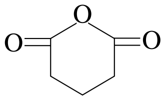
11. 

Final product (Z) will be:

(1) 

(2) 

(3) 

(4) 

12. Which of the following statements is wrong?

(1) Formic acid is a stronger acid than acetic acid

(2) o-Bromobenzoic acid is a weaker acid than o-chlorobenzoic acid.

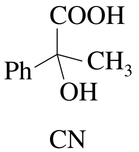
(3) Lactic acid does not respond positively to silver mirror test with Tollens reagent

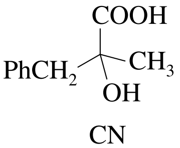
(4) Benzaldehyde does not reduce Fehling's solution

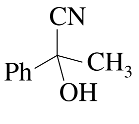
13. In a set of reactions, acetic acid yielded a product (D).

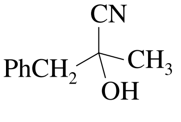
$$CH_3COOH \xrightarrow{SOCl_2} (A) \xrightarrow[anhyd.\ AlCl_3]{benzene} (B) \xrightarrow{HCN} (C) \xrightarrow[heat]{H_3O^+} (D)$$

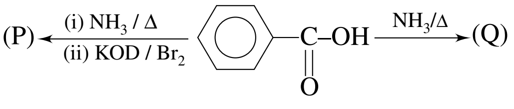
The structure of (D) would be

(1) 

(2) 

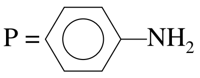
(3) 

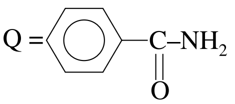
(4) 

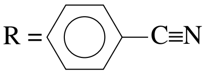
14. 

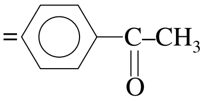
$$\xrightarrow{P_2O_5} (R) \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ CH_3MgBr} (S) \xrightarrow[(ii)\ H^+/\Delta]{(i)\ H_2NOH} T + U$$

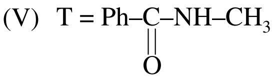
Which of following are correct?

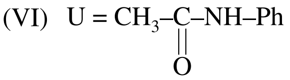
(I) 

(II) 

(III) R =


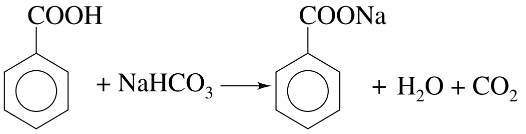
(IV) S =


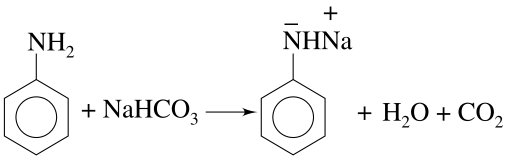
(V)

$T = Ph{-}\underset{\underset{O}{\|}}{C}{-}NH{-}CH_3$

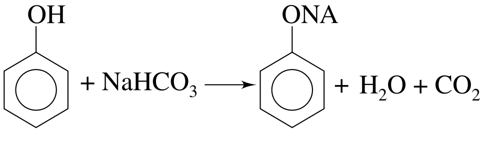
(VI)

$U = CH_3{-}\underset{\underset{O}{\|}}{C}{-}NH{-}Ph$

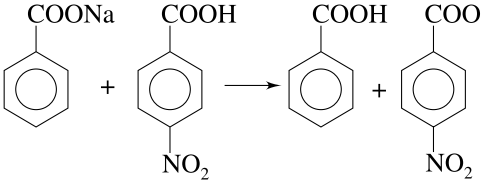
(1) I, II, III, IV only (2) II, III, IV, V, VI
(3) I, III, IV, V (4) All are correct

15. Which of the following reactions are feasible (practically possible)?

(I)


(II)


(III)


(IV)


(1) I, II (2) II, III
(3) III, IV (4) I, IV

16. Carboxylic acid, although unreactive to alcohols, reacts in the presence of small amount of conc. H_2SO_4 or with 2-3% of HCl?

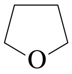
(I) This reaction is called Fischer esterification reaction.
(II) The equilibrium is shifted to R.H.S. if H_2O is removed by azeotropic distillation with benzene.
(III) The reaction of RCOCl and R′OH to give ester (RCOOR′) is irreversible and more feasible than Esterification of RCOOH.
(IV) If the above esterification of RCOOH is carried out in excess of R′OH, the equilibrium is shifted to R.H.S.

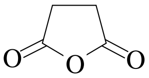
(1) (I), (II) (2) (I), (II), (III)
(3) (I), (II), (IV) (4) (I), (II), (III), (IV)

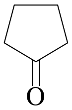
17. An ester (A) with molecular formula $C_9H_{10}O_2$ was treated with excess of CH_3MgBr and the complex so formed was treated with H_2SO_4 to give a olefin (B). Ozonolysis of (B) gave a ketone with molecular formula C_8H_8O which shows positive iodoform test. The Structure of (A) is

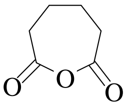
(1) $C_6H_5COOC_2H_5$
(2) $CH_3COCH_2COC_6H_5$
(3) p–CH_3O–C_6H_4–$COCH_3$
(4) $C_6H_5COOC_6H_5$

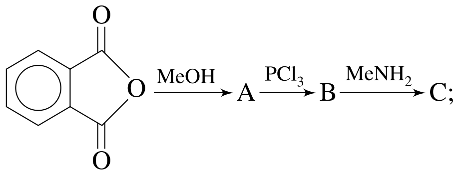
18. Which of the following products is formed when adipic acid is heated?

(1)


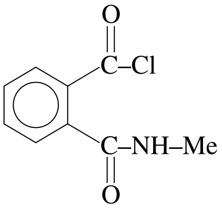
(2)


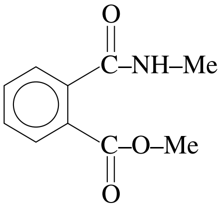
(3)


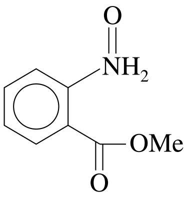
(4)


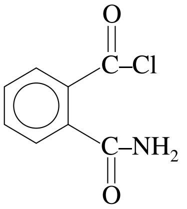
19.


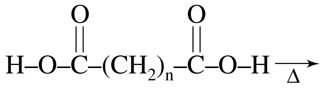
Product (C) of the reaction is:

(1)


(2)


(3)


(4)


20.

$H{-}O{-}\overset{\overset{O}{\|}}{C}{-}(CH_2)_n{-}\overset{\overset{O}{\|}}{C}{-}O{-}H \xrightarrow[\Delta]{}$ Product, At what value of (n) given compound will not evolve CO_2 gas:

(1) n = 5 (2) n = 4
(3) n = 2 (4) n = 1

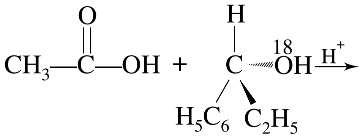
EXERCISE 3

One and More Than One Option Correct Type Question

1. Which reagent(s) given below can be used to separate a mixture of butanol and butanoic acid from its ethereal solution?

(1) $NaNH_2$ (aq) (2) NH_3 (aq)
(3) NaOH (4) $NaHCO_3$

2. Consider the following Fischer esterification reaction



A pure enantiomer

The correct statement is/are

(1) O^{18} will be a part of ester

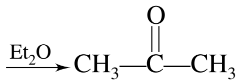
(2) Alcohol will retain its configuration

(3) O^{18} will be sp^2-hybridised in ester

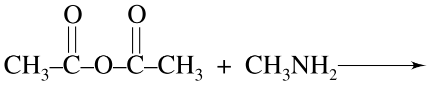
(4) Sign of specific rotation of ester is same as that of alcohol

3. Which is/are not a suitable nucleophilic substitution reaction?

(1) $CH_3COCl + CH_3MgBr$/ (excess)

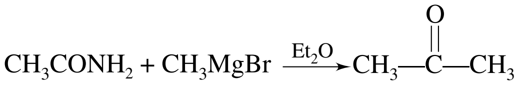


$\xrightarrow{Et_2O} CH_3—\overset{O}{\overset{||}{C}}—CH_3$

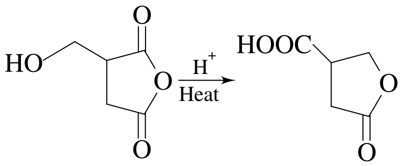
(2) 

$CH_3–\overset{O}{\overset{||}{C}}–O–\overset{O}{\overset{||}{C}}–CH_3 + CH_3NH_2 \longrightarrow$

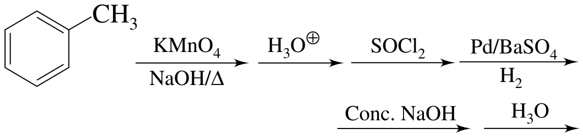
$CH_3–CONHCH_3+CH_3COOH$

(3) 

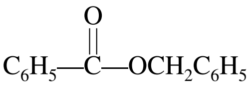
$CH_3CONH_2 + CH_3MgBr \xrightarrow{Et_2O} CH_3—\overset{O}{\overset{||}{C}}—CH_3$

(4) 

4. Consider the reaction sequence in the following synthesis



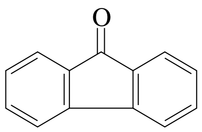
The end product (s) is/are

(1) 

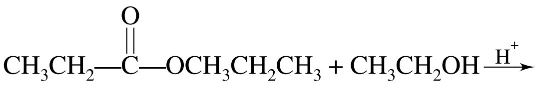
$C_6H_5—\overset{O}{\overset{||}{C}}—OCH_2C_6H_5$

(2) C_6H_5COOH

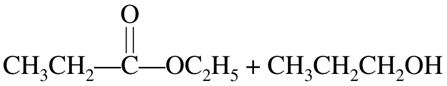
(3) $C_6H_5CH_2OH$

(4) 

5. The correct statement regarding the following transformation is/are



$CH_3CH_2—\overset{O}{\overset{||}{C}}—OCH_3CH_2CH_3 + CH_3CH_2OH \xrightarrow{H^+}$



$CH_3CH_2—\overset{O}{\overset{||}{C}}—OC_2H_5 + CH_3CH_2CH_2OH$

(1) Presence of excess of ethanol favours the reaction

(2) Both acid and base can act as catalyst

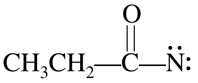
(3) Smaller alcohols always displace the larger alcohols from ester

(4) The reaction is second order in both acid and base catalysed condition

6. In the reaction given below, the intermediates formed is/are

$CH_3CH_2CONH_2 + NaOH + Br_2 \longrightarrow CH_3CH_2NH_2$

(1) $CH_3CH_2CONHBr$

(2) 

$CH_3CH_2—\overset{O}{\overset{||}{C}}—\ddot{N}:$

(3) $CH_3CH_2CONHOH$

(4) CH_3CH_2NCO

Statement Type Question

(1) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(2) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(3) Statement-1 is True, Statement-2 is False.

(4) Statement-1 is False, Statement-2 is True.

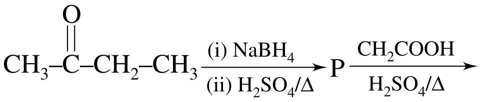
7. **Statement-1:** α, α′-dichloro acetic acid does not undergo haloform reaction

Statement-2: α, α′-dichloro acetic acid has alpha-hydrogen.

8. **Statement I:** CH_3COOH when treated with $C_2H_5\overset{18}{O}H/H^+$, $CH_3CO\overset{18}{O}C_2H_5$ is formed.

Statement II: In Fischer esterification, protonated acid undergoes nucleophilic attack by alcohol in the slow, rate determining step.

9. **Statement I:** In the following reaction,



$CH_3–\overset{O}{\overset{||}{C}}–CH_2–CH_3 \xrightarrow[\text{(ii) } H_2SO_4/\Delta]{\text{(i) } NaBH_4} P \xrightarrow[H_2SO_4/\Delta]{CH_3COOH}$

Racemic mixture of esters

Statement II: Alcohol (P) undergoes nucleophilic addition on protonated acetic acid.

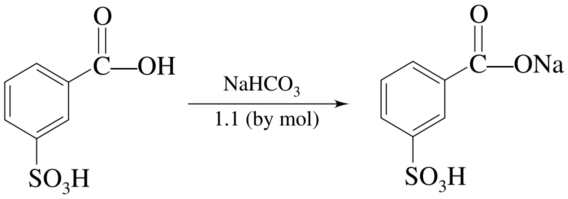
10. **Statement I:** Ester formation from acid and alcohol occur in acidic medium but not in alkaline medium. However, hydrolysis of esters proceeds in both acidic and alkaline medium.

Statement II: In alkaline medium carboxylic acid in neutralised into salt which do not undergo nucleophilic attack by alcohols.

11. Statement I: *p*-nitrobenzoic acid is more reactive than benzoic acid in acid catalysed esterification reaction.

Statement II: Rate determining step in Fischer's esterification reaction of carboxylic acid in nucleophilic attack by alcohols on protonated acid.

12. Statement I: Consider the following neutralisation reaction,



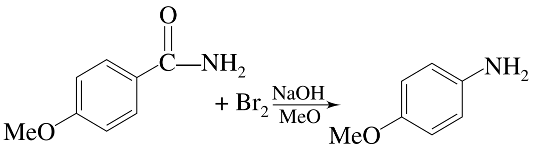
Statement II: —SO_3H is an electron withdrawing group, increased the acidity of —COOH.

13. Statement I: Acetyl chloride (CH_3COCl) undergoes faster nucleophilic substitution reaction (S_N2) than chloroethane.

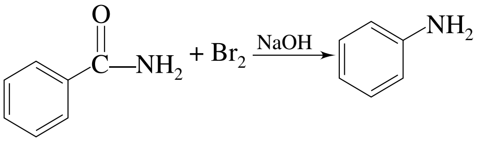
Statement II: In acetyl chloride, the leaving group (—Cl) is in resonance with the carbonyl (>C=O) group.

14. Statement I: Consider the following two amides undergoing Hofmann's bromamide reaction.

I.



II.



Reaction (I) occurs more easily than (II).

Statement II: the rate determining step in Hofmann's bromamide reaction is unimolecular elimination of bromide (Br^-) forming isocyanate.

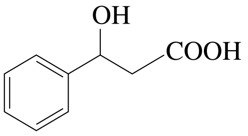
Comprehension Type Question

Passage based questions (Q. 15–17)

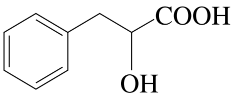
An organic compound A ($C_9H_{10}O_3$) is optically active. A changes orange colour of CrO_3–H_2SO_4 solution to blue–green. A on vigorous oxidation with hot, concentrated, alkaline $KMnO_4$ gives benzoic acid. Also A on treatment with HBr gives B ($C_9H_9O_2Br$) with same configuration as that of A.

15. What is the structure of A?

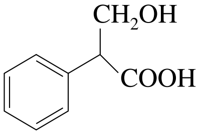
(1)



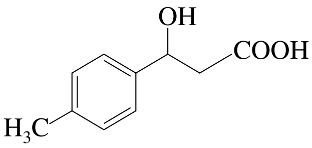
(2)



(3)



(4)

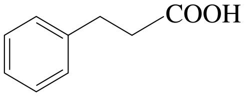


16. Consider the following reaction,

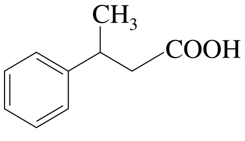
$$B \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) NaOH}} \xrightarrow[\text{Heat}^+]{H_3PO_4} \xrightarrow[H_2]{[(C_6H_5)_3P]_3\,RhCl} C$$

The structure of C is

(1)



(2)



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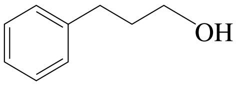
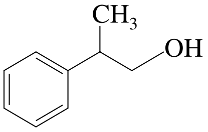


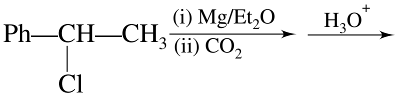
(4)



17. Which of the following sequence of reaction gives C as the major product?

(1) $Ph—CH_2CH_2Cl \xrightarrow[Et_2O]{Mg} \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CO_2}$

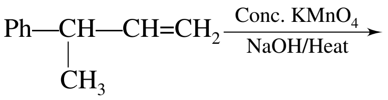
(2)



$Ph—\underset{\underset{Cl}{|}}{CH}—CH_3 \xrightarrow[\text{(ii) } CO_2]{\text{(i) Mg/Et}_2\text{O}} \xrightarrow{H_3O^+}$

(3) $Ph—CH_2CH_2—CH=CH_2 \xrightarrow[H_2O_2]{O_3}$

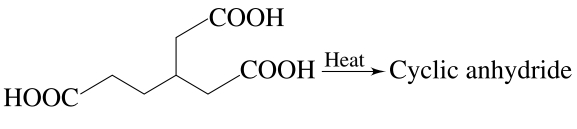
(4)



$Ph—\underset{\underset{CH_3}{|}}{CH}—CH=CH_2 \xrightarrow[\text{NaOH/Heat}]{\text{Conc. KMnO}_4}$

Single Digit Integer Type Question

18. Consider the following reaction



How many carbon atoms are present in the ring of cyclic anhydride?

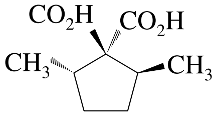
19. How many different isomers exist for $C_3H_6O_2$ which reduces Tollens' reagent as well as forms $C_5H_8O_3$ upon treatment with acetic anhydride?

20. How many amide isomer sexist for C_4H_9ON that do not form amine on treatment with Br_2-NaOH?

21. How many different isomers of $C_4H_{11}N$ on heating with CS_2 followed by the addition of $HgCl_2$ gives alkyl isothiocyanide (RNCS)?

22. If a mixture containing ethyl acetate and ethyl propanoate is refluxed with C_2H_5ONa/C_2H_5OH, ester condensation takes place. How many different condensation would be formed?

23.

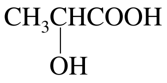


How many product will be formed when above compound undergo de-carboxylation?

EXERCISE 4

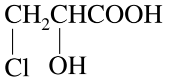
1. End product of the following reaction is **(AIEEE 2002)**

$$CH_3CH_2COOH \xrightarrow[\text{Red P}]{Cl_2} \xrightarrow{\text{Alcoholic KOH}}$$

(1) 
$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCOOH$

(2) 
$\underset{\displaystyle OH}{\underset{|}{C}}H_2CH_2COOH$

(3) $CH_2{=}CHCOOH$

(4) 
$\underset{\displaystyle Cl}{\underset{|}{C}}H_2\underset{\displaystyle OH}{\underset{|}{C}}HCOOH$

2. In the anion $HCOO^-$ the two carbon–oxygen bonds are found to be of equal length. What is the reason for it? **[AIEEE-2003]**

(1) The anion $HCOO^-$ has two resonating structures

(2) The anion is obtained by removal of a proton from the acid molecule

(3) Electronic orbitals of carbon atom are hybridised

(4) The C=O bonds is weaker than the C—O bond

3. Ethyl isocyanide on hydrolysis in acidic medium generates **(AIEEE 2003)**

(1) ethylamine salt and methanoic acid

(2) propanoic acid and ammonium salt

(3) ethanoic acid and ammonium salt

(4) methylamine salt and ethanoic acid

$$C_2H_5NC + H_2O \xrightarrow{H^+} \underset{\text{Fromic acid}}{HOOCH} + C_2H_5NH_2$$

$$C_2H_5NH_2 + H^+ \longrightarrow \underset{\text{Salt}}{C_2H_5NH_3^+}$$

4. When $CH_2{=}CH—COOH$ is reduced with $LiAlH_4$, the compound obtained will be **(AIEEE 2003)**

(1) $CH_3—CH_2—COOH$ (2) $CH_2{=}CH—CH_2OH$

(3) $CH_3—CH_2—CH_2OH$ (4) $CH_3—CH_2—CHO$

5. The general formula $C_nH_{2n}O_2$ could be for open chain **(AIEEE 2003)**

(1) Diketones (2) Carboxylic acids

(3) Diols (4) Dialdehydes

6. Which one of the following does not have sp^2 hybridised carbon? **[AIEEE-2004]**

(1) Acetone (2) Acetic acid

(3) Acetonitrile (4) Acetamide

7. A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was **(AIEEE 2005)**

(1) CH_3OH (2) HCHO

(3) CH_3COCH_3 (4) CH_3COOH

8. The compound formed as a result of oxidation of ethyl benzene by $KMnO_4$ is **[AIEEE-2007]**

(1) Benzophenone (2) Acetophenone

(3) Benzoic acid (4) Benzyl alcohol

9. Sodium ethoxide has reacted with ethanoyl chloride. The compound that is produced in the above reaction is **(AIEEE 2011)**

(1) diethyl ether (2) 2-butanone

(3) ethyl chloride (4) ethyl ethanoate

10. The strongest acid amongst the following compounds is **(AIEEE 2011)**

(1) CH_3COOH

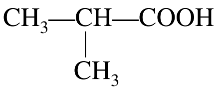
(2) HCOOH

(3) $CH_3CH_2CH(Cl)CO_2H$

(4) $ClCH_2CH_2CH_2COOH$

11. An organic compound A upon reacting with NH_3 gives B. On heating, B gives C. C in the presence of KOH reacts with Br_2 give $CH_3CH_2NH_2$. A is **(JEE Main 2013)**

(1) CH_3COOH (2) $CH_3CH_2CH_2COOH$

(3) 
$CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}H—COOH$ (4) CH_3CH_2COOH

12. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is

(JEE Main 2013)

(1) 2 (2) 5

(3) 4 (4) 6

13. In the reaction,

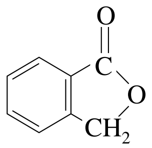
$$CH_3COOH \xrightarrow{LiAlH_4} A \xrightarrow{PCl_5} B \xrightarrow{alc.\ KOH} C$$

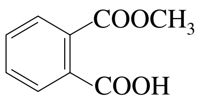
the product C is **(JEE Main 2014)**

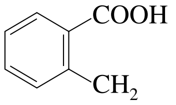
(1) Acetaldehyde (2) Acetylene

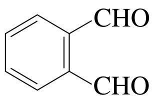
(3) Ethylene (4) Acetyl chloride

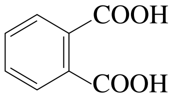
14. Which of the following reactants on reaction with conc. NaOH followed by acidification gives following lactone as the: **[IIT-2006]**



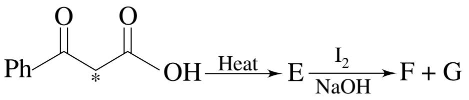
(1) 

(2) 

(3) 

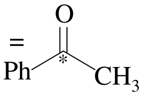
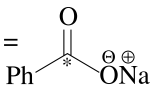
(4) 

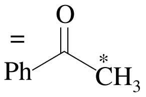
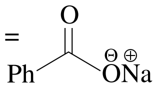
15. In the following reaction sequence, the correct structures of E, F and G are

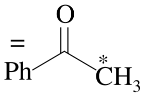
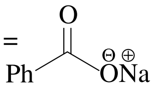


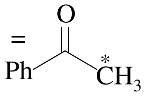
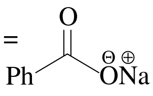
(* implies ^{13}C labelled carbon)

(2008, Only One Options Correct Type)

(1) E =  F =  $G = CHI_3$

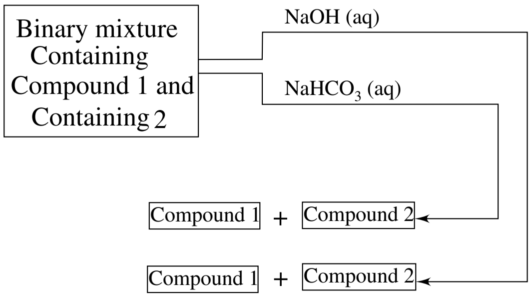
(2) E =  F =  $G = CHI_3$

(3) E =  F =  $G = \overset{*}{C}HI_3$

(4) E =  F =  $G = \overset{*}{C}HI_3$

16. Identify the binary mixture(s) that can be separated into individual compounds, by differential extraction, as shown in the given scheme.

(2012, One or More than One Options Correct Type)



(1) C_6H_5OH and C_6H_5COOH

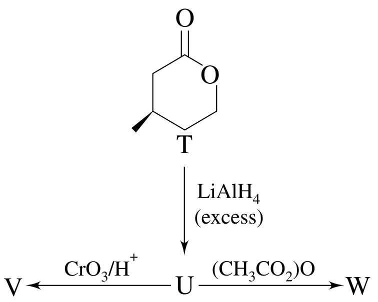
(2) C_6H_5COOH and $C_6H_5CH_2OH$

(3) $C_6H_5CH_2OH$ and C_6H_5OH

(4) $C_6H_5CH_2OH$ and $C_6H_5CH_2COOH$

17. With reference to the scheme given, which of the given statement(s) about T, U, and W is(are) correct?

(2012, One or More than One Options Correct Type)



(1) T is soluble in hot aqueous NaOH

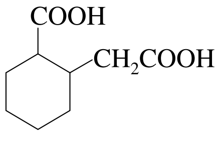
(2) U is optically active

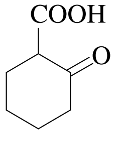
(3) Molecular formula of W is $C_{10}H_{18}O_4$

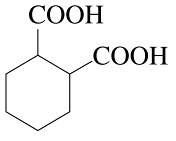
(4) V gives effervescence on treatment with aqueous $NaHCO_3$

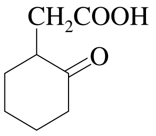
18. The compound that undergoes decarboxylation most readily under mild condition is

(2012, Only One Option Correct Type)

(1) 

(2) 

(3) 

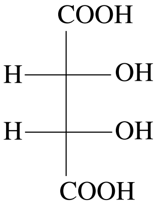
(4) 

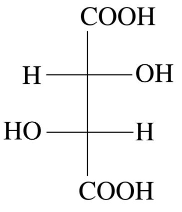
Passage Based Questions: (Q. 19 and 20)

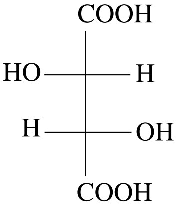
P and Q are isomers of dicarboxylic acid $C_4H_4O_4$. Both decolourise Br_2/H_2O. On heating. P form the cyclic anhydride.

Upon treatment with dilute alkaline $KMnO_4$. P as well as Q could produce one or more than one forms S, T and U

(2013 Adv., Comprehension Type)


5


T


U

19. Compounds formed from P and Q, respectively, are:

(1) Optically active S and optically active pair (T, U)

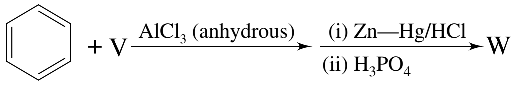
(2) Optically inactive S and optically inactive pair (T, U)

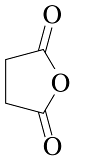
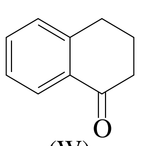
(3) Optically active pair (T, U) and optically active S

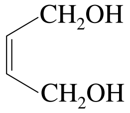
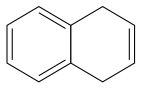
(4) Optically inactive pair (T, U) and optically inactive S

20. In the following reaction sequences V and W, respectively, are

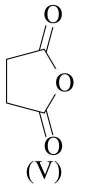
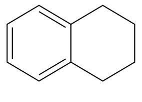
$$Q \xrightarrow[\Delta]{H_2/Ni} V$$



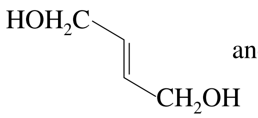
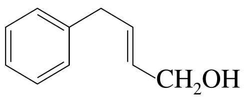
(1)  and  (W)

(2)  and 

(V) (W)

(3)  and 

(V) (W)

(4)  and 

(V) (W)

21. The compound that does not liberate CO_2, on treatment with aqueous sodium, is

(2013 Adv., Only One Option Correct Type)

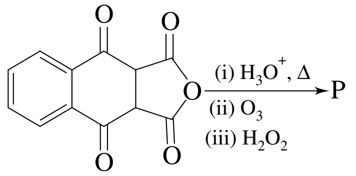
(1) Benzoic acid

(2) Benzenesulphonic acid

(3) Salicylic acid

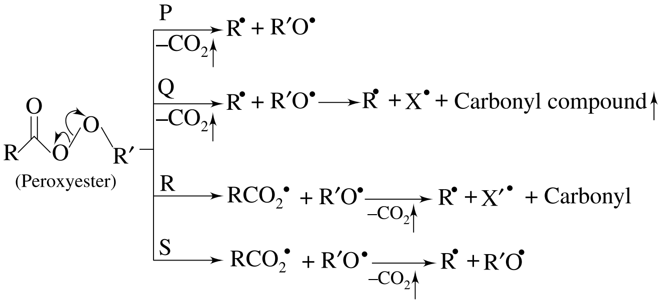
(4) Carbolic acid (Phenol)

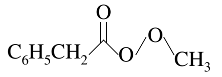
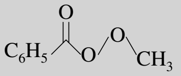
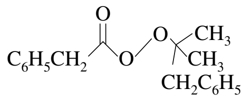
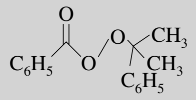
22. The total number of carboxylic acid group in the product P is **(2013 Adv., Integer Type)**



23. Different possible thermal decomposition pathways for peroxyesters are shown below. Match each pathway from Column I with an appropriate structure in Column II and select the correct answer using the code given below the lists.

(2014 Adv., Matching Type)



	Column I		Column II
I.	Pathway P	p.	
II.	Pathway Q	q.	
III.	Pathway R	r.	
IV.	Pathway S	s.	

Codes

	I	II	III	IV
(1)	p	r	s	q
(2)	q	s	r	p
(3)	s	p	q	r
(4)	r	q	p	s

ANSWER KEY

EXERCISE # 1

1. (2) 2. (3) 3. (1) 4. (2) 5. (2)
6. (3) 7. (4) 8. (1) 9. (2) 10. (4)
11. (2) 12. (1) 13. (3) 14. (2) 15. (2)
16. (2) 17. (1) 18. (3) 19. (4) 20. (3)
21. (1) 22. (3) 23. (1) 24. (1) 25. (2)

EXERCISE # 2

1. (3) 2. (3) 3. (3) 4. (3) 5. (2)
6. (1) 7. (2) 8. (3) 9. (2) 10. (2)
11. (4) 12. (2) 13. (1) 14. (2) 15. (4)
16. (4) 17. (1) 18. (3) 19. (2) 20. (3)

EXERCISE # 3

1. (3,4) 2. (1,2) 3. (1,3) 4. (2,3)
5. (1,2,4) 6. (1,4) 7. (2) 8. (1) 9. (2)
10. (1) 11. (1) 12. (4) 13. (2) 14. (2)
15. (3) 16. (2) 17. (2) 18. (5) 19. (4)
20. (6) 21. (5) 22. (6) 23. (1)

EXERCISE # 4

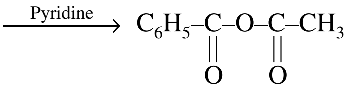
1. (3) 2. (1) 3. (1) 4. (2) 5. (2)
6. (3) 7. (4) 8. (3) 9. (4) 10. (3)
11. (4) 12. (2) 13. (3) 14. (3) 15. (3)
16. (2,4) 17. (1.3.4) 18. (2) 19. (2) 20. (1)
21. (4) 22. (2) 23. (1)

HINT AND SOLUTION

EXERCISE # 1

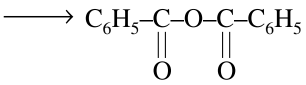
1. [2]

(i) $C_6H_5COOH + CH_3COCl$



$$\xrightarrow{\text{Pyridine}} C_6H_5\text{–}\underset{\underset{O}{\|}}{C}\text{–}O\text{–}\underset{\underset{O}{\|}}{C}\text{–}CH_3$$

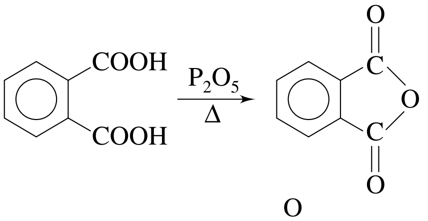
(ii) $C_6H_5COO^{\ominus}Na^{\oplus} + C_6H_5COCl$



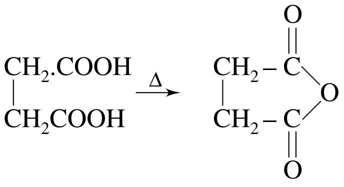
$$\longrightarrow C_6H_5\text{–}\underset{\underset{O}{\|}}{C}\text{–}O\text{–}\underset{\underset{O}{\|}}{C}\text{–}C_6H_5$$

(iii) $C_6H_5ONH_2 + CH_3COO^{\ominus}\ Na^{\oplus} \longrightarrow$ no anhydride $–NH_2$ is poor leaving group, so SN reaction does not take place.

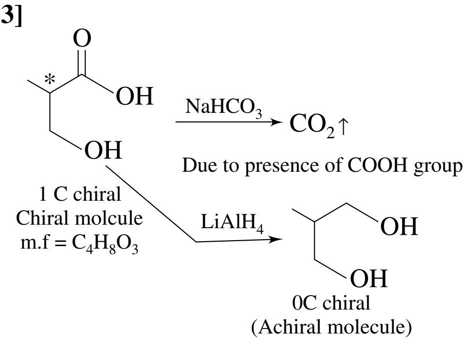
(iv)



(v)



2. [3]



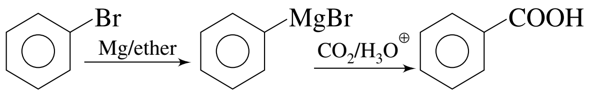
3. [1]

Rate of hydrolysis ∝ power of leaving tendency ∝ $\dfrac{1}{\text{Base strength}}$ (for acid derivative via SN_2 reaction)

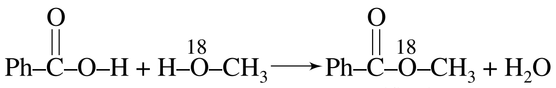
$Cl^{\ominus}$	$\overset{\ominus}{O}$–R	$\overset{\ominus}{N}H_2$	$\overset{\ominus}{O}\text{–}\overset{\overset{O}{\|}}{C}\text{–}R$
	EN factor		Resonance
size↑	EN↑	EN↓	B.S↓
B.S↓	B.S↓	B.S↑	L.g↑
L.g↑	L.g↑	L.g↓	

Order of factor
Size, resonance, EN
(I) > (IV) > (II) > (III)

4. [2]



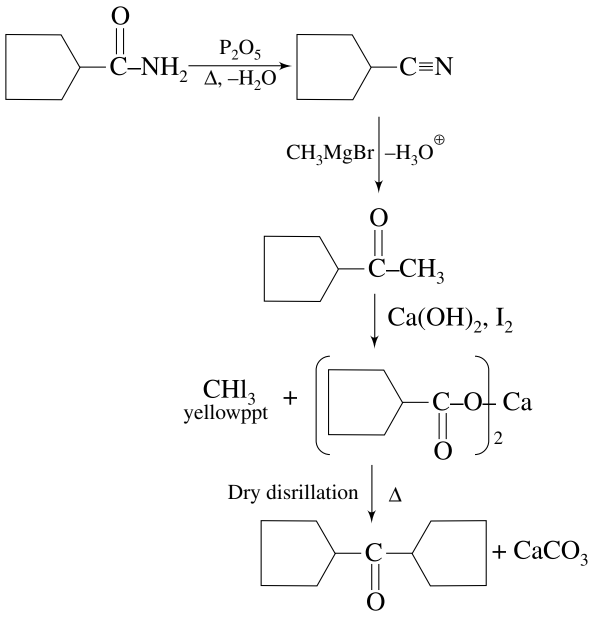
5. [2]



$$Ph\text{–}\overset{\overset{O}{\|}}{C}\text{–}O\text{–}H + H\text{–}\overset{18}{O}\text{–}CH_3 \longrightarrow Ph\text{–}\overset{\overset{O}{\|}}{C}\text{–}\overset{18}{O}\text{–}CH_3 + H_2O$$

Estrification

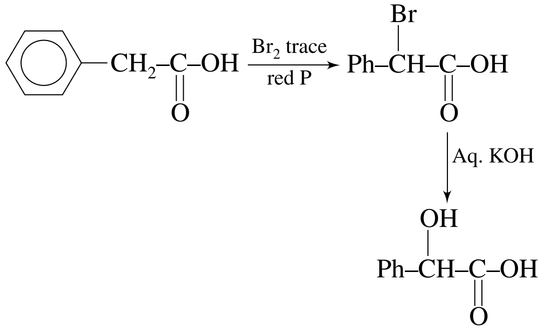
6. [3]



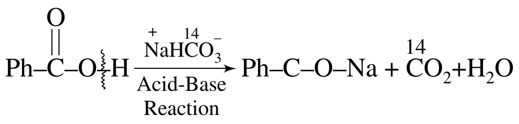
7. [4]

Carboxylic acid having at least one α-H, will give HVZ reaction.

8. [1]

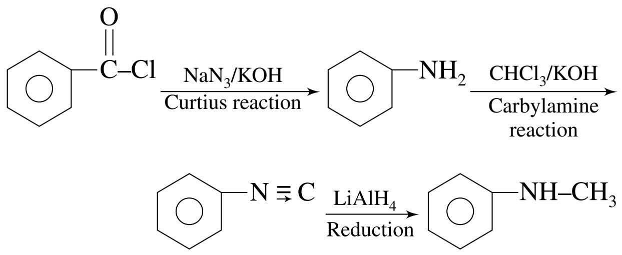


9. [2]

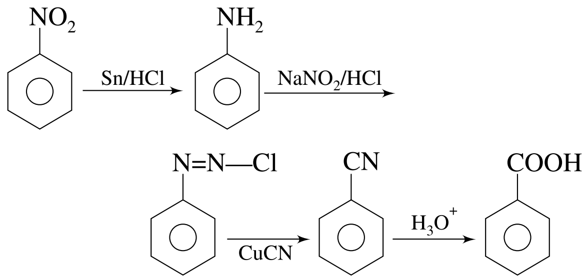


$$Ph-\overset{\overset{O}{\|}}{C}-O-H \xrightarrow[\text{Acid-Base Reaction}]{\overset{+}{Na}H\overset{14}{C}O_3^-} Ph-C-O-Na + \overset{14}{C}O_2 + H_2O$$

10. [4]



11. [2]

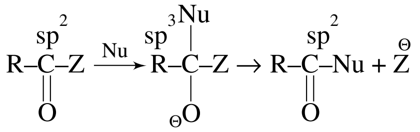


12. [1]

$$R-OH \xrightarrow[{[Rh(CO)_2I_2]^-}]{CO} R-COOH$$

Gurbet reaction

13. [3]



$$R-\overset{sp^2}{\underset{\underset{O}{\|}}{C}}-Z \xrightarrow{Nu} R-\overset{\overset{Nu}{|}}{\underset{\underset{{}^{\ominus}O}{|}}{\overset{sp^3}{C}}}-Z \rightarrow R-\overset{sp^2}{\underset{\underset{O}{\|}}{C}}-Nu + \overset{\ominus}{Z}$$

14. [2]

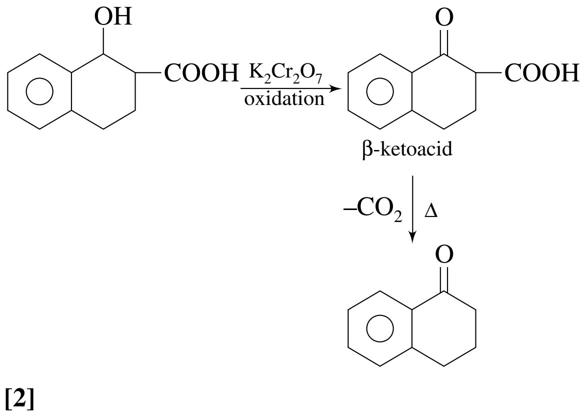
When nucleophilic site belongs to same period than Nucleophilic strength ∝ base strength

$CH_3-\underset{\underset{O}{\|}}{C}-O^{\ominus}$	$\overset{\ominus}{O}H$	$\overset{\ominus}{N}H_2$
–ve charge delocalised Less basic Less N.S.	E.N ↑ B.S ↓ N.S ↓	E.N ↓ B.S ↑ N.S ↑

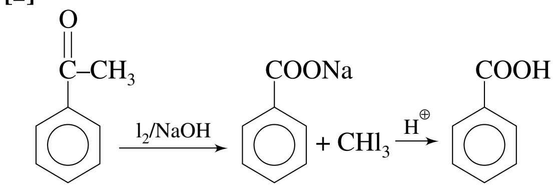
thus correct order is

$CH_3-COO^- < \overset{\ominus}{O}H < \overset{\ominus}{N}H2$

15. [2]



16. [2]

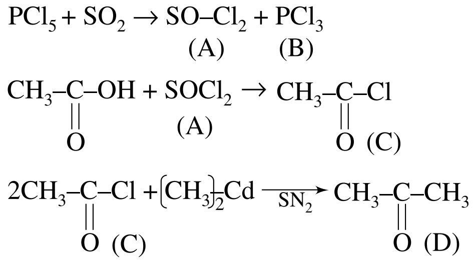


Acetophenone Benzoic acid

17. [1]

For acyl substitution base strength of Nu:$^-$ greater than LG.

18. [3]

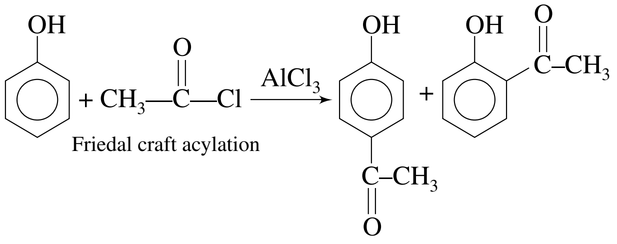


$PCl_5 + SO_2 \rightarrow \underset{(A)}{SO\text{–}Cl_2} + \underset{(B)}{PCl_3}$

$CH_3\text{–}\underset{O}{\underset{\|}{C}}\text{–}OH + \underset{(A)}{SOCl_2} \rightarrow CH_3\text{–}\underset{O\ (C)}{\underset{\|}{C}}\text{–}Cl$

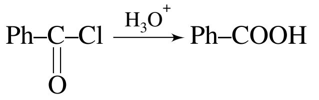
$2CH_3\text{–}\underset{O\ (C)}{\underset{\|}{C}}\text{–}Cl + \left[CH_3\right]_2Cd \xrightarrow[SN_2]{} CH_3\text{–}\underset{O\ (D)}{\underset{\|}{C}}\text{–}CH_3$

19. [4]



20. [3]

$Ph\text{–}CN \xrightarrow{H_3O^+} Ph\text{–}COOH$



$Ph\text{–}\underset{O}{\underset{\|}{C}}\text{–}Cl \xrightarrow{H_3O^+} Ph\text{–}COOH$

$Ph\text{–}CH_2\text{–}Cl \xrightarrow{H_3O^+} Ph\text{–}CH_2\text{–}OH$

$Ph\text{–}COO\text{–}CH_3 \xrightarrow{H_3O^+} Ph\text{–}COOH$

21. [1]

$CH_3CH_2ONa \xrightarrow[\text{Pressure (ii)} H^+]{\text{(i) CO, }\Delta} CH_3\text{–}CH_2\text{–}COONa$

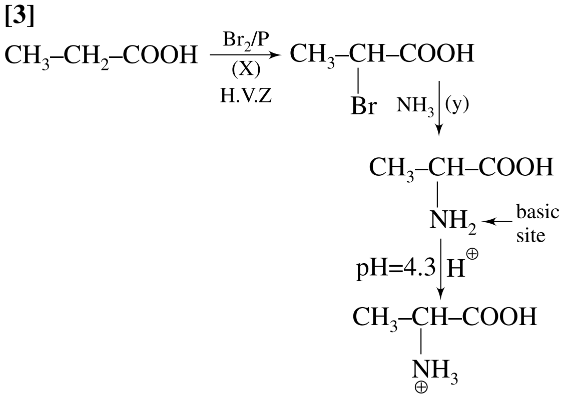
$\xrightarrow{H^+} CH_3\text{–}CH_2\text{–}COOH$

$CH_2 = CH_2 + CO + H_2O \xrightarrow[670°C]{H_3P0_4}$

Carboxylation

$CH_3\text{–}CH_2\text{–}COOH$

22. [3]



$CH_3\text{–}CH_2\text{–}COOH \xrightarrow[\text{(X)}]{Br_2/P} CH_3\text{–}\underset{Br}{\underset{|}{CH}}\text{–}COOH$

H.V.Z

$\downarrow NH_3\ (y)$

$CH_3\text{–}\underset{NH_2}{\underset{|}{CH}}\text{–}COOH$ ← basic site

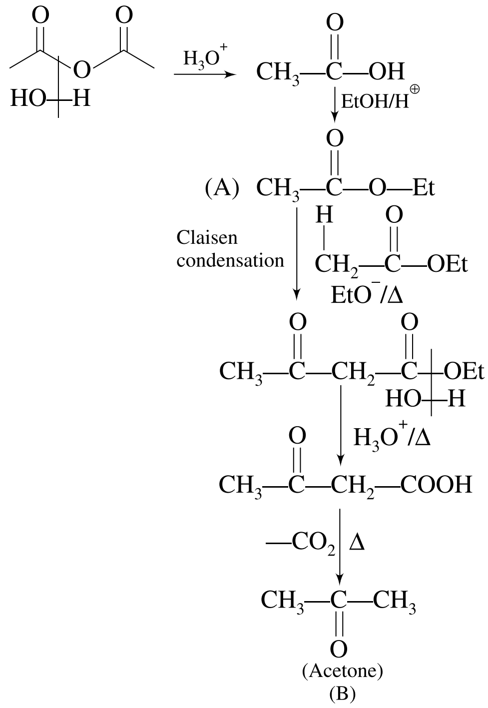
$\downarrow pH=4.3\ H^{\oplus}$

$CH_3\text{–}\underset{\underset{\oplus}{N}H_3}{\underset{|}{CH}}\text{–}COOH$

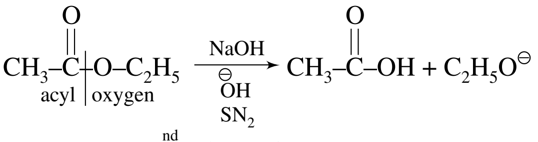
23. [1]

Theory based

24. [1]



25. [2]

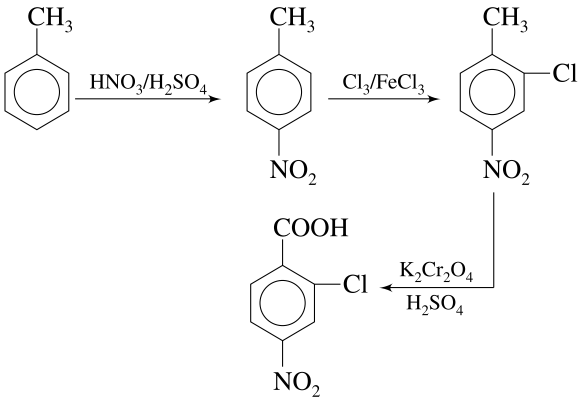


$CH_3\text{–}\overset{O}{\overset{\|}{\underset{\text{acyl}}{C}}}\mid\underset{\text{oxygen}}{O\text{–}C_2H_5} \xrightarrow[\overset{\ominus}{O}H\ \ SN_2]{NaOH} CH_3\text{–}\overset{O}{\overset{\|}{C}}\text{–}OH + C_2H_5O^{\ominus}$

(2nd order reaction)

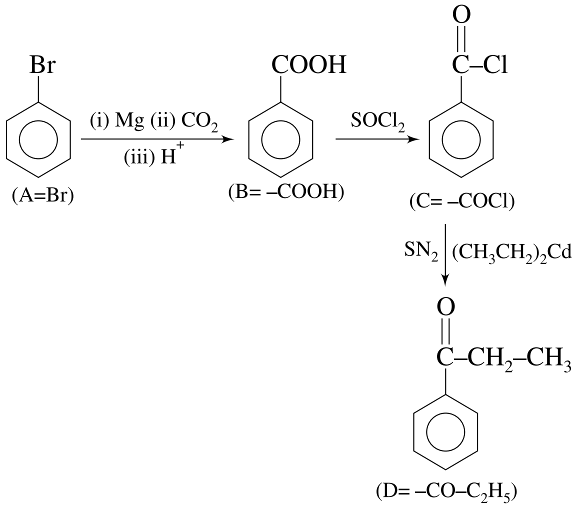
EXERCISE # 2

1. [3]



2–chloro-4-nitro benzoicacid

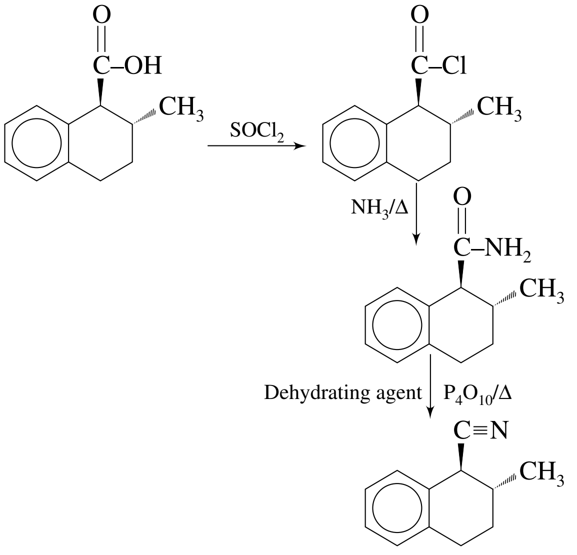
2. [3]



3. [3]

$$CO_2 + H_2 \xrightarrow[\Delta]{H_2SO_4} H\text{–}COOH \xrightarrow[H_2SO_4]{\text{Conc.}} CO + H_2O$$

4. [2]



5. [2]

Rate of hydrolysis for same gr. (S_N2 reaction) ∝ EWG ∝ $\frac{1}{\text{ERG}}$

Thus (II) > (IV) > (I) > (III)

6. [1]

Acid + alcohol ⟶ ester

(±) (+) (+ +) & (– +)

7. [2]

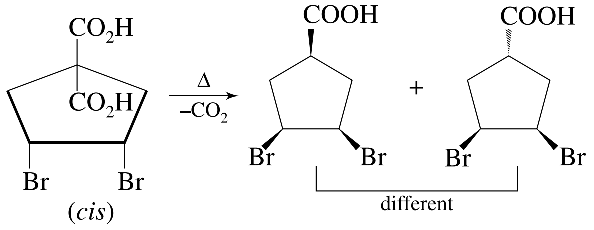
$$BaCO_3 + H_2SO_4 \longrightarrow CO_2\,(x)$$

$$CH_2{=}CH\text{–}Br \xrightarrow{\text{Mg/THF}} CH_2{=}CH\text{–}MgBr$$

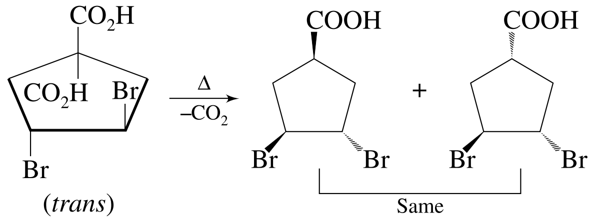
$$\Big\downarrow \; CO_2(X),\; H_3O^+$$

$$CH_2{=}CH\text{–}COOH$$

8. [3]

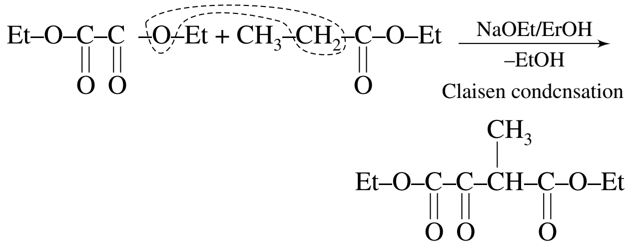


(*cis*)

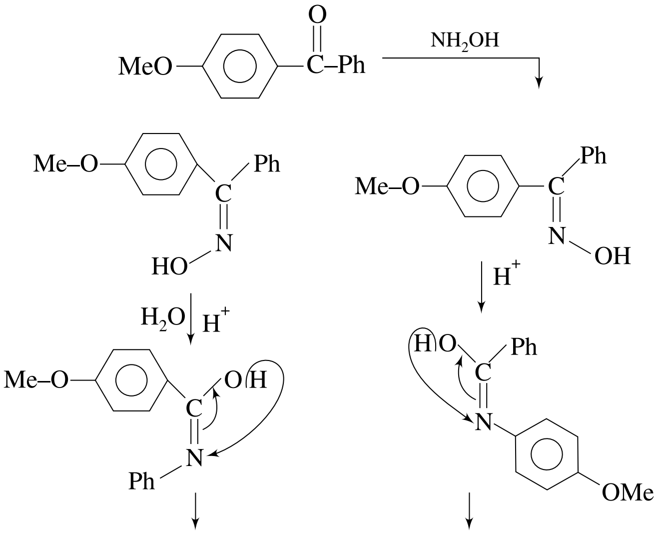


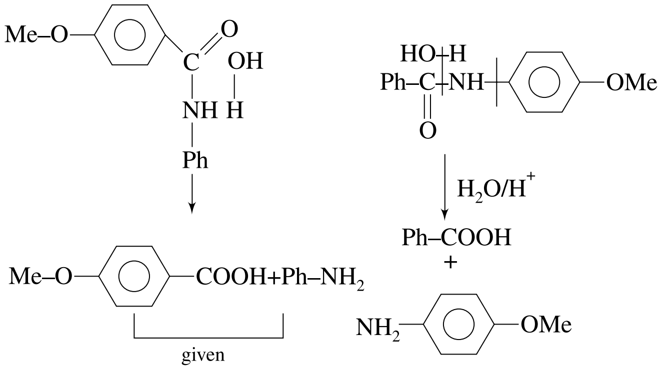
(*trans*)

9. [2]

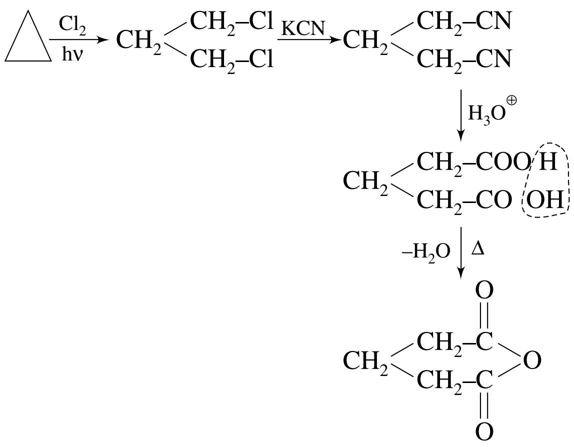


10. [2]





11. [4]

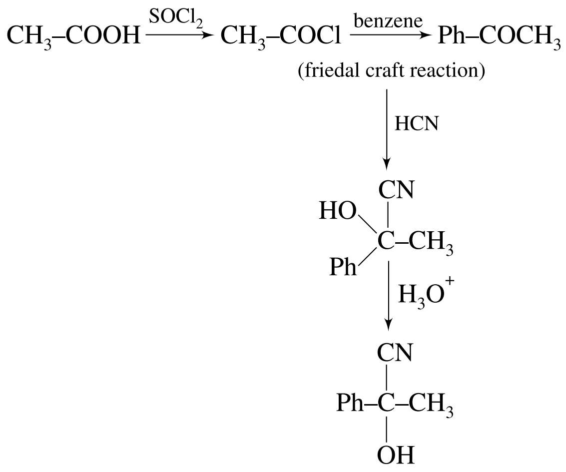


12. [2]

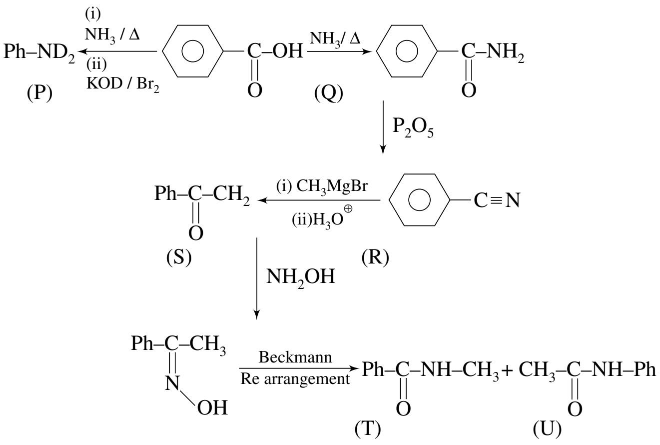
(1) HCOOH is more acidic than acidic acid due to presence of ERG (CH_3) in acetic acid.

(2) o-bromobenzoic acid is more acidic than o-chloro benzoic acid due to ortho effect so it is wrong given (3) & (4) are also correct (refer key concept).

13. [1]



14. [2]



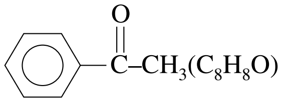
15. [4]

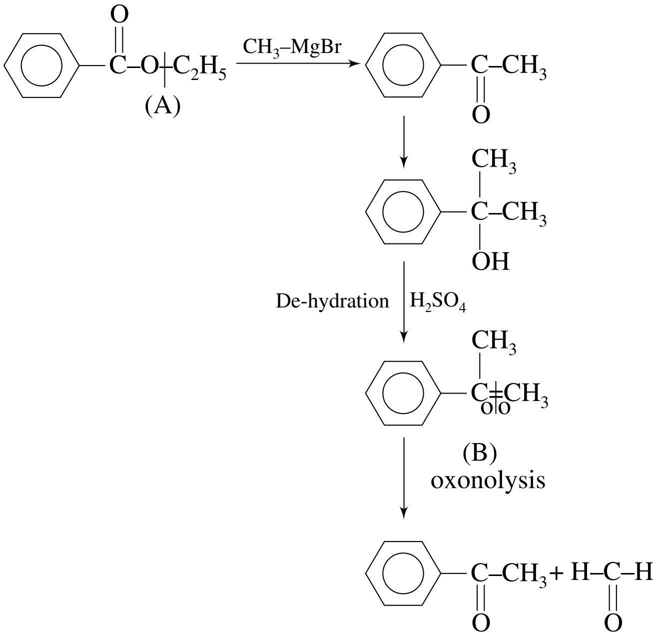
16. [4]

17. [1]

$$\underset{\text{Ester}}{C_9H_{10}O_2\ (A)} \xrightarrow[H_2SO_4]{CH_3-MgBr} \underset{\text{olefin}}{(B)} \xrightarrow{\text{ozonolysis}} \underset{\substack{\text{Ketone}\\ \text{+ve iodoform test}}}{C_8H_8O}$$

Thus, Ketone should be

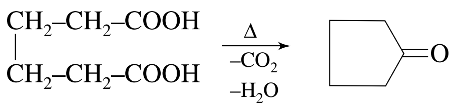




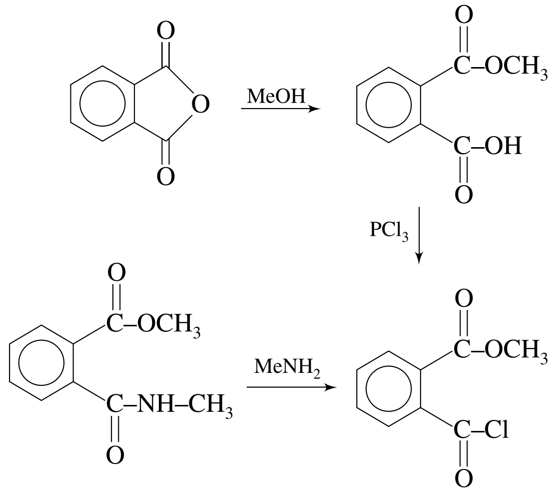
Gives +ve iodoform test

18. [3]

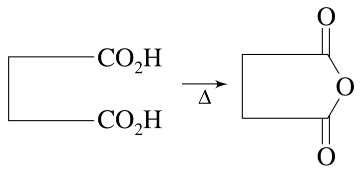
Removal of both CO_2 and H_2O takes place



19. [2]



20. [3]



Succinic acid on heating form anhydride.

EXERCISE # 3

One and more than one option correct type question

1. [3,4]

Both NaOH and $NaHCO_3$ form salt with butanoic acid but not with butanol.

2. [1,2]

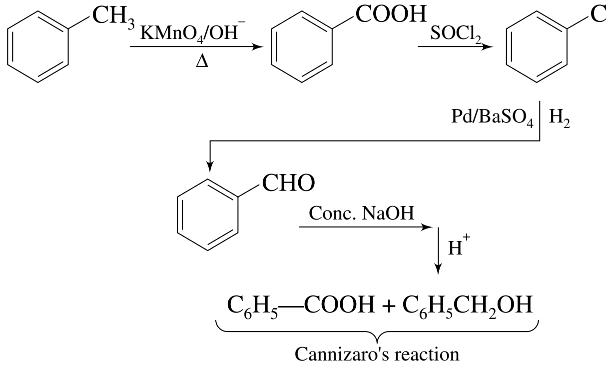
During esterification (Fischer), nucleophilic attack occur from sp^3 oxygen of alcohol, hence configuration of α-carbon of alcohol is retained.

3. [1,3]

(1) Grignard reagent attack further on ketone.

(3) Grignard reagent takes $H^{\oplus}$ from amide.

4. [2,3]



5. [1,2,4]

(1) Excess of ethanol drive the equilibrium in forward direction (Le Chatelier's principle).

(2) Transesterification proceeds well in both acidic and basic medium.

(3) It is wrong, condition can be made suitable so that even larger alcohol can replace the smaller one.

(4) In the presence of acid or base catalyst, reaction is always bimolecular second order.

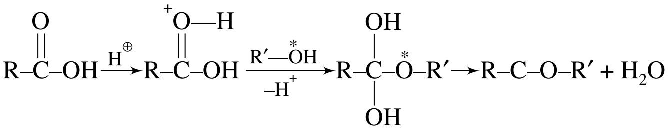
6. [1, 4]

In Hofmann's bromamide degradation, N-bromamide is formed in the first step and isocyanate is formed in the slow rate determining step. Nitrine and hydroxamic acids are not formed.

Statement Type Question

7. [2]

8. [1]



$$R-\overset{\overset{O}{||}}{C}-OH \xrightarrow{H^{\oplus}} R-\overset{\overset{^{+}O-H}{||}}{C}-OH \xrightarrow[-H^{+}]{R'-\overset{*}{O}H} R-\underset{OH}{\overset{OH}{\overset{|}{\underset{|}{C}}}}-\overset{*}{O}-R' \rightarrow R-C-O-R' + H_2O$$

9. [2]

Both are independently correct but formation of racemic mixture of esters is due to the formation of racemic mixture of alcohols (P) by hydride ion attack on planar carbonyl carbon of butanone.

10. [1]

RCOOH is neutralised to RCOONa which itself is a nucleophile and it does not undergo nucleophilic attack by poor nucleophile ROH.

11. [1]

Electron withdrawing nitro group increases electrophilic character of —COOH, hence increases reactivity in Fischer's esterification.

12. [4]

—SO_3H is more acidic than —COOH, hence sulphonic acid group would be neutralised first.

13. [2]

Both are correct but greater reactivity of acid chloride is due to sp^2-hybridised carboxyl carbon and greater electrophilic character of the same.

14. [2]

Electron releasing methoxy group from para position increases the reactivity in Hofmann's reaction

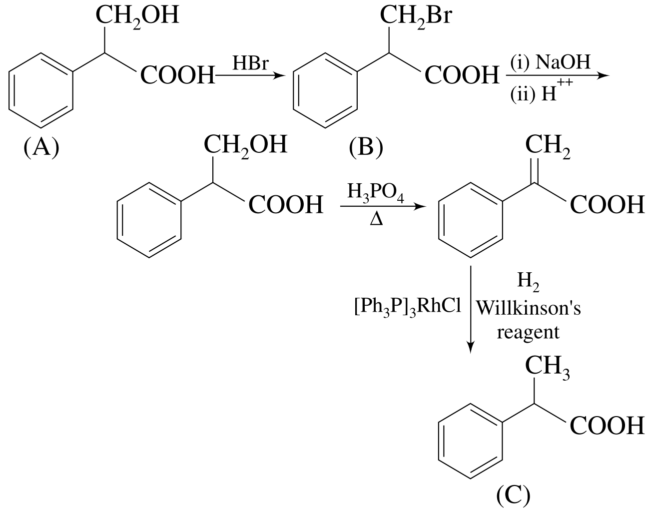
Comprehension type question

Passage Based Questions (17 to 19)

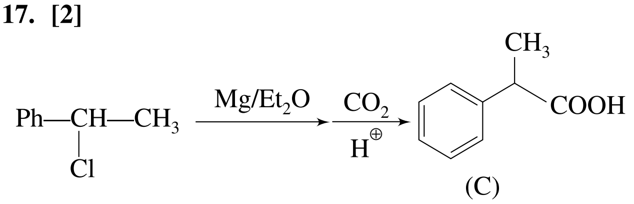
15. **[3]**

From the above discussion, structure of A satisfying all the criteria of option 3.

16. **[2]**

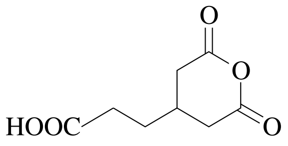


17. **[2]**

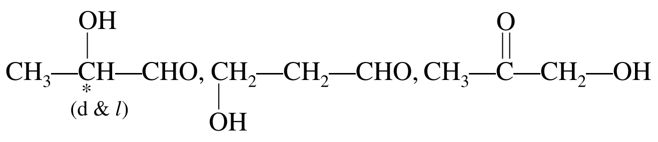


Single Digit Integer Type Question

18. **[5]**



19. **[4]**

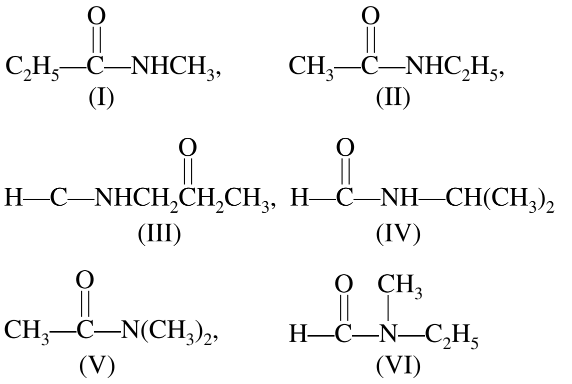


$\underset{(d \,\&\, l)}{CH_3-\underset{*}{\overset{\overset{OH}{|}}{C}}H-CHO}$, $\underset{\underset{OH}{|}}{CH_2}-CH_2-CHO$, $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-OH$

α-hydroxy ketones also reduces Tollens' reagent.

20. **[6]**

2° and 3° amine isomers do not form amine on treatment with Br_2 + NaOH.



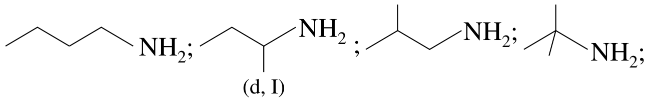
$\underset{\text{(I)}}{C_2H_5-\overset{\overset{O}{\|}}{C}-NHCH_3}$, $\underset{\text{(II)}}{CH_3-\overset{\overset{O}{\|}}{C}-NHC_2H_5}$,

$\underset{\text{(III)}}{H-\overset{\overset{O}{\|}}{C}-NHCH_2CH_2CH_3}$, $\underset{\text{(IV)}}{H-\overset{\overset{O}{\|}}{C}-NH-CH(CH_3)_2}$

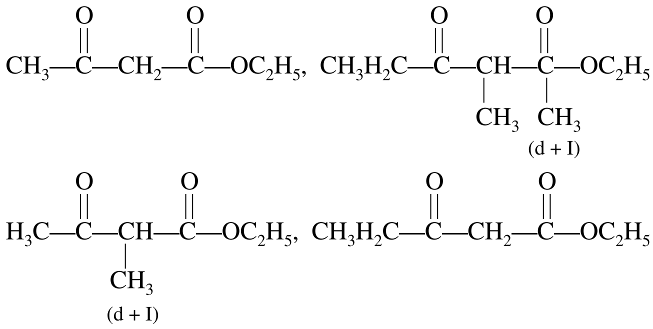
$\underset{\text{(V)}}{CH_3-\overset{\overset{O}{\|}}{C}-N(CH_3)_2}$, $\underset{\text{(VI)}}{H-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{N}-C_2H_5}$

21. **[5]**

It is mustard oil reaction which is given by primary amines only.



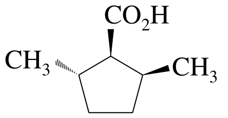
22. **[6]**



$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5$, $\underset{\text{(d + I)}}{CH_3H_2C-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{\overset{\overset{O}{\|}}{C}}-OC_2H_5}$

$\underset{\text{(d + I)}}{H_3C-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OC_2H_5}$, $CH_3H_2C-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5$

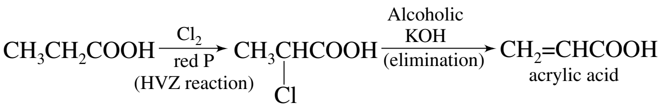
23. **[1]**



Only one product will obtained.

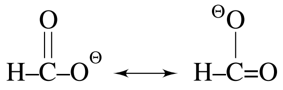
EXERCISE # 4

1. **[3]**



$CH_3CH_2COOH \xrightarrow[\text{red P}]{Cl_2} \underset{\text{(HVZ reaction)}}{} CH_3\underset{\underset{Cl}{|}}{C}HCOOH \xrightarrow[\text{(elimination)}]{\text{Alcoholic KOH}} \underset{\text{acrylic acid}}{CH_2{=}CHCOOH}$

2. **[1]**



$H-\overset{\overset{O}{\|}}{C}-O^{\ominus} \longleftrightarrow H-\overset{\overset{^{\ominus}O}{|}}{C}=O$

equal contributed canonical form

3. **[1]**

$C_2H_5NC + H_2O \xrightarrow{H^+} \underset{\text{Formic acid}}{HOOCH + C_2H_5NH_2}$

$C_2H_5NH_2 + H^+ \longrightarrow \underset{\text{Salt}}{C_2H_5NH_3^+}$

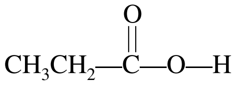
4. [2]

$LiAlH_4$ reduces —COOH to —CH_2OH without affecting C=C bond.

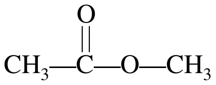
5. [2]

$C_nH_{2n}O_2$ is general formula for open chain carboxylic acids and esters.

e.g., n = 3 $C_3H_6O_2$



Acid $CH_3CH_2—\overset{\overset{O}{||}}{C}—O—H$



Ester $CH_3—\overset{\overset{O}{||}}{C}—O—CH_3$

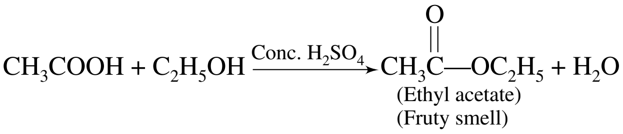
6. [3]

$\underset{sp^3}{CH_3}—\underset{sp}{C} \equiv N$

7. [4]

A liquid + $C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4}$ Compound (Fruity smell)

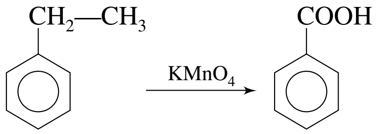
Fruity smell is the characteristic property of ester, thus the above reaction leads to the formation of ester.



$$CH_3COOH + C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} \underset{\substack{\text{(Ethyl acetate)} \\ \text{(Fruty smell)}}}{CH_3\overset{\overset{O}{||}}{C}—OC_2H_5} + H_2O$$

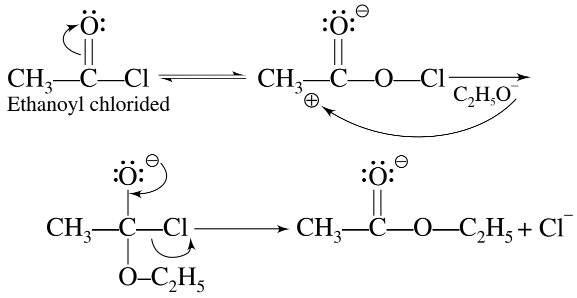
This reaction is called esterification.

8. [3]



9. [4]

$C_2H_5O^-Na^+ \rightleftharpoons C_2H_5O^- + Na^+$



$Na^+ + Cl^- \longrightarrow NaCl$

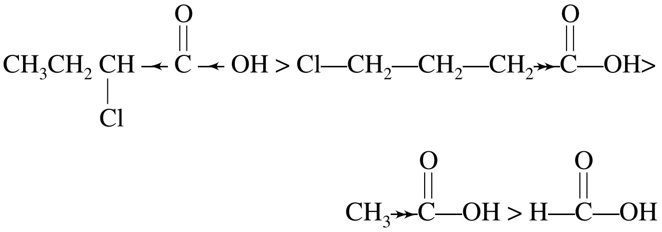
This is by S_N reaction Cl^- is a better leaving group than $C_2H_5O^-$ and then ethyl ethanoate is formed.

10. [3]

–I effect exerting (electron withdrawing) groups increase the acidic strength of an acid by withdrawing electron density towards itself, thereby weakening O—H bond and thus, the release of H^+ ion by an acid becomes easier.

Whereas +I effect excreting (e^- releasing) groups decreases the acidic strength by donating electron density to O-atom.

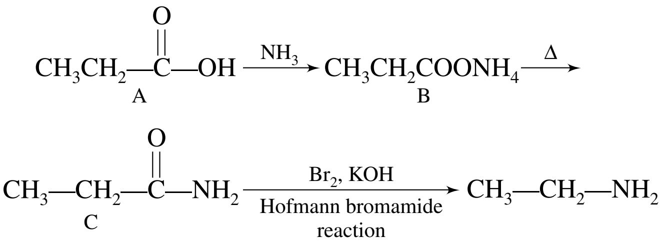
Further, –I effect decreases with distance. Thus, the acidic strength off the given acids would be:



$$CH_3CH_2\underset{\underset{Cl}{|}}{CH} \leftarrow \overset{\overset{O}{||}}{C} \leftarrow OH > Cl—CH_2—CH_2—CH_2 \twoheadrightarrow \overset{\overset{O}{||}}{C}—OH >$$
$$CH_3 \twoheadrightarrow \overset{\overset{O}{||}}{C}—OH > H—\overset{\overset{O}{||}}{C}—OH$$

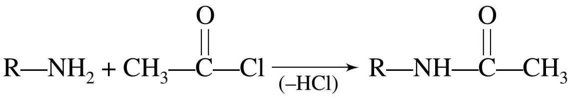
Hence, $CH_3CH_2\underset{\underset{Cl}{|}}{CH}—\overset{\overset{O}{||}}{C}—OH$ is most acidic and strongest acid than other given compounds.

11. [4]



$$\underset{A}{CH_3CH_2—\overset{\overset{O}{||}}{C}—OH} \xrightarrow{NH_3} \underset{B}{CH_3CH_2COONH_4} \xrightarrow{\Delta}$$
$$\underset{C}{CH_3—CH_2—\overset{\overset{O}{||}}{C}—NH_2} \xrightarrow[\text{Hofmann bromamide reaction}]{Br_2,\ KOH} CH_3—CH_2—NH_2$$

12. [2]

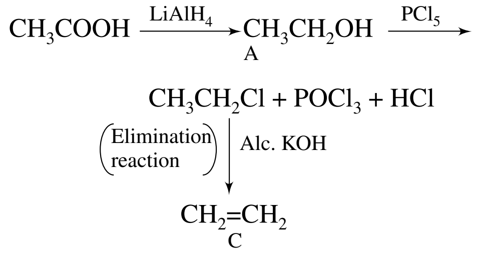


$$R—NH_2 + CH_3—\overset{\overset{O}{||}}{C}—Cl \xrightarrow[(-HCl)]{} R—NH—\overset{\overset{O}{||}}{C}—CH_3$$

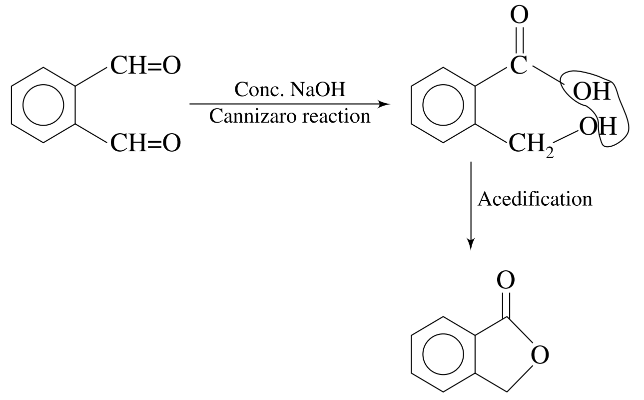
Since, each —$COCH_3$ group displace one H-atom in the reaction of one mole $CH_3—\overset{\overset{O}{||}}{C}—Cl$ with one —NH_2 group, the molecular mass increases with 42 unit, Since, the mass increases by (390–180) = 210, hence the number of —NH_2 group is $\frac{210}{42} = 5$.

13. [3]

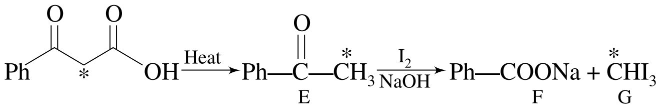
The complete series of reaction can be represented as



14. [3]



15. [3]



16. [2,4]

For separation be differential extraction one of the component must form salt with the given base so that the salt will be extracted in aqueous layer leaving other component in organic layer.

(1) Both phenol and benzoic acid form salt with NaOH, hence this mixture cannot be separated.

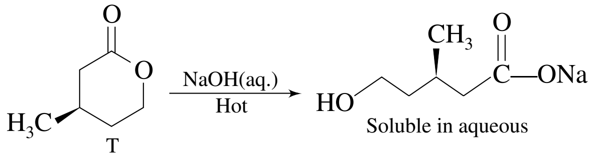
(2) Benzoic acid forms salt with NaOH while benzyl alcohol does not, hence the mixture can be separated using NaOH. Also benzoic acid forms salt with $NaHCO_3$ but benzyl alcohol does not, hence $NaHCO_3$ can be used for separation.

(3) Neither benzyl alcohol nor phenol forms salt with $NaHCO_2$, mixture cannot be separated using $NaHCO_3$

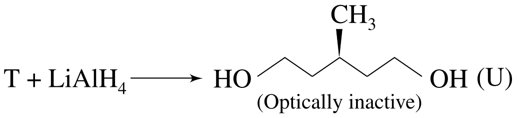
(4) $C_6H_5CH_2COOH$ forms salt with NaOH; $C_6H_5CH_2OH$ does not. Hence mixture can be separated using NaOH.·$C_6H_5CH_2COOH$ forms salt with $NaHCO_3$. but $C_6H_5CH_2OH$ does not; hence mixture can be separated using $NaHCO_3$.

17. [1,3,4]

(1) Undergoes an ester hydrolysis in hot aqueous alkali as

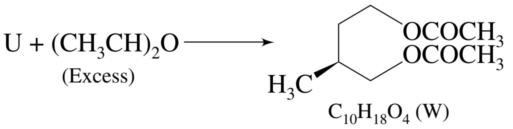


(2) $LiAlH_4$ reduces ester to alcohol as

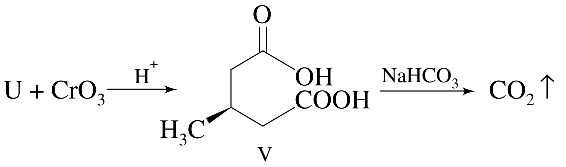


"U" No chiral carbon optically inactive.

(3) U on treatment with excess of acetic anhydride forms a disaster as

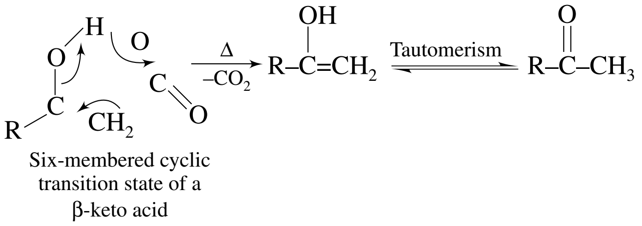


(4) U on treatment with CrO_3H^+ undergoes oxidation to diacid which gives effervescence with $NaHCO_3$.



18. [2]

It is a β-keto acid which undergo decarboxylation in very mild condition, i.e., on simple heating. This occurs through a six-membered cyclic transition state as:



Note (t) (i) Ordinary carboxylic acid require soda time catalyst for decorboxylation

(ii) Final step of decarboxylation in the above shown mechanism involve tatutomerism, therefore, for decarboxylation of β-keto acid by above mechanism, the acid must contain an α-H

Passage Based Questions: (20-21)

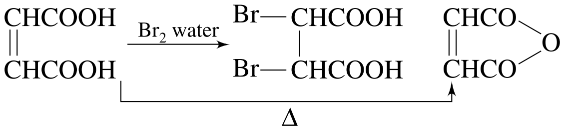
19. [2]

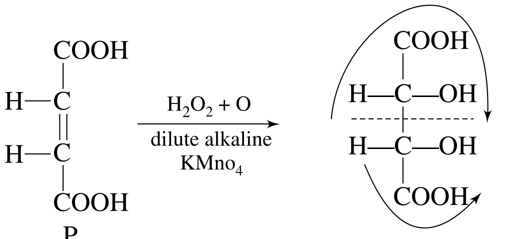
P, Q $\xrightarrow{Br_2\text{ water}}$ Decolourised

P and Q have (C = C) bond

$P \xrightarrow{\Delta} \text{Anhydride}$

Thus, P is *cis*-isomer

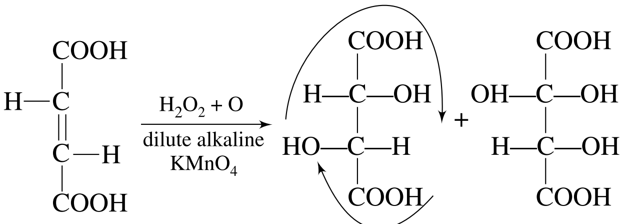




P
(Maleric acid)

S

Optically inactive due to internal compensation of rotation (meso-somer)



Q
Fumaric acid

T, d (+)

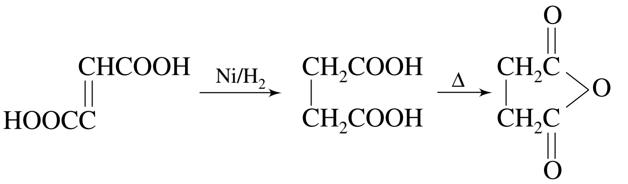
U, I (–)

T and U (in 1 : 1 molar ratio) form optically inactive (racemic mixture) due to external compensation

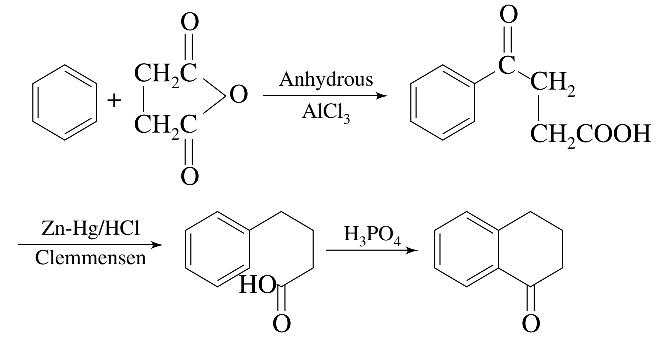
20. [1]

Plan Ni/H_2 reduces (C = C) bond

Benzene undergoes Friedel–Crafts reaction Zn–Hg/HCl reduces carbonyl group (Clemmensen reduction)



Succinic anhydride (v)



W

21. [4]

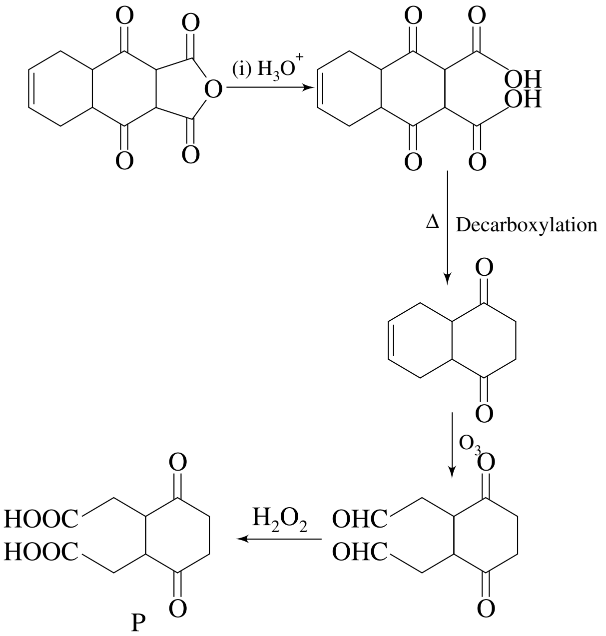
$NaHCO_3 \rightleftharpoons Na^+ + HCO_3^-$ HCO_3^- is decomposed by acid releasing CO_2

$$HCO_3^- + H^+ \longrightarrow H_2O + CO_2$$

If acid is stronger than HCO_3^- then CO_2 is released. Phenol is less acidic and thus, does not liberate CO_2 with $NsaHCO_3$.

22. [2]

Plan Reactant is cyclic anhydride and changes to dicarboxylic acid on hydrolysis. Also there is decarboxylation on heating if there is keto group w.r.t —COOH group. Ozonolysis cleaves (C=C) bond and H_2O_2 oxidises —CHO to —COOH group.



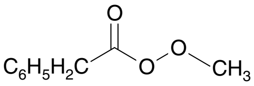
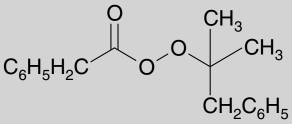
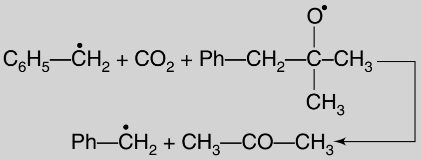
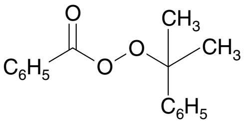
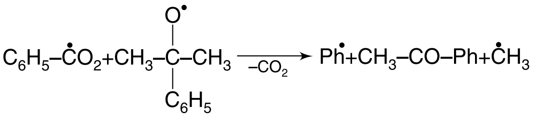
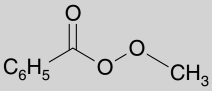
P

Thus, number of —COOH groups in P = 2.

23. [1]

The problem can be solved by using the stability of radical obtained after fragmentation of peroxyester. Allylic radical are more stable than alkyl radical, so when there is a possibility of formation of allyl radical, it will undergo fragmentation through formation of allyl radical, i.e., fragmentation produces stable radical.

One the basis of stability of radical, fragmentation can be done as:

	Column I	Column II	Explanation
i.	p.		$C_6H_5-\dot{C}H_2 + CO_2 + CH_3\dot{O}$
ii.	r.		 $C_6H_5-\dot{C}H_2 + CO_2 + Ph-CH_2-\overset{O^{\bullet}}{\underset{CH_3}{C}}-CH_3 \rightarrow Ph-\dot{C}H_2 + CH_3-CO-CH_3$
iii.	s.		 $C_6H_5-\dot{C}O_2+CH_3-\overset{O^{\bullet}}{\underset{C_6H_5}{C}}-CH_3 \xrightarrow[-CO_2]{} \dot{Ph}+CH_3-CO-Ph+\dot{C}H_3$
iv.	t.		$C_6H_5-\dot{C}O_2 + \dot{C}H_3O$ $\rightarrow C_6H_5^{\bullet} + CO_2$