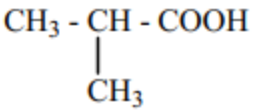
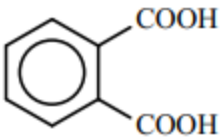
CHAPTER - 21

CARBOXYLIC ACIDS

SYNOPSIS

Saturated monocarboxylic acids form a homologous series which has a general formula $C_nH_{2n+1}COOH$ or $C_nH_{2n}O_2$

In the IUPAC system, aliphatic carboxylic acids are named as 'alkanoic acid'.

	Formula	Common Name	IUPAC name
1.	$CH_3–CH_2–COOH$	Propionic acid	Propanoic acid
2.	$CH_3–CH_2–CH_2–COOH$	Butyric acid	Butanoic acid
3.		Isobutyric acid	2-methyl propanoic acid
4.	$CH_3–(CH_2)_3–COOH$	Valeric acid	Pentanoic acid
5.	$CH_3–(CH_2)_4–COOH$	Caproic acid	Hexanoic acid
6.	$HOOC–CH_2–COOH$	Malonic acid	Propane-1,3-dioic acid
7.	$HOOC–(CH_2)_2–COOH$	Succinic acid	Butane-1,4-dioic acid
8.	$HOOC–(CH_2)_3–COOH$	Glutaric acid	Pentane-1,5-dioic acid
9.	$HOOC–(CH_2)_4–COOH$	Adipic acid	Hexane-1,6-dioic acid
10.	$C_6H_5–COOH$	Benzoic acid OR (Benzoic acid)	Benzene carboxylic acid
11.		Phthalic acid	Benzene-1,2-dicarboxylic acid

Structure & Isomerism

In –COOH group, carboxyl carbon undergoes sp^2–hybridisation. The geometry around the carboxyl carbon is trigonal planar and the bond angle is nearly 120°.

The carboxylic C is less electrophilic than carbonyl C due to resonance.

- The carboxylic acids exhibit chain, position, functional and stereo isomerism.
- Esters are functional isomers of carboxylic acids.
- Optical isomerism is observed in Lactic acid.
- Fumaric acid and maleic acids are geometrical isomers.

Methods of preparation

I. Oxidation of 1° Alcohols, aldehydes & ketones

1° ROH are readily oxidised to acids with $KMnO_4$ in neutral, acidic or basic medium or with $K_2Cr_2O_7$ and with CrO_3 in acidic medium

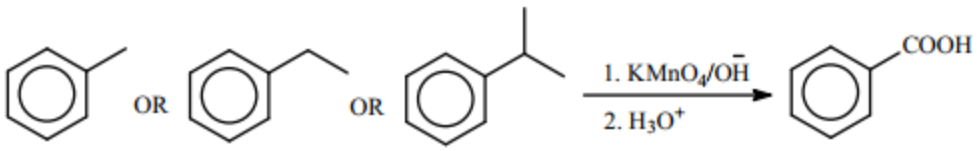
$$R-CH_2-OH \xrightarrow{KMnO_4/OH^{(-)}} R-COOH$$

$$\underset{\text{Decan}-1-\text{ol}}{CH_3-(CH_2)_8-CH_2-OH} \xrightarrow{CrO_3-H_2SO_4} \underset{\text{Decanoic acid}}{CH_3-(CH_2)_8-COOH}$$

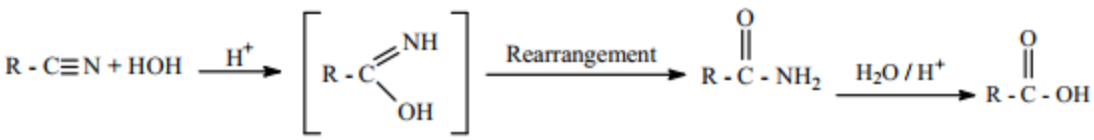
- Aldehydes are more easily oxidised to acids on treatment with oxidising agents such as HNO_3, $KMnO_4$, $K_2Cr_2O_7$ etc. Even mild oxidising agents like Tollens and Fehling's oxidise aldehyde.
- Ketones are oxidised by strong oxidising agents at elevated temperature.

II From alkyl benzenes :

Side chain oxidation of alkyl benzenes with chromic acid or acidic or alkaline $KMnO_4$ gives acids. The entire side chain is oxidised to –COOH group . 1° and 2° alkyl groups are oxidised in the same manner, while 3° group is not affected.



III Hydrolysis of Nitriles



unstable imidol

- Hydrolysis can be done with alkali also
- HCN on hydrolysis forms formic acid

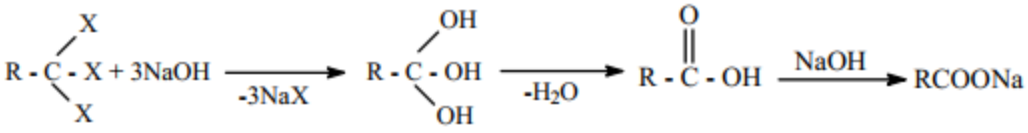
IV. Hydrolysis of ester, acyl halides and anhydrides

$$R-COOR^1 + HOH \xrightarrow{HCl} RCOOH + R^1OH$$

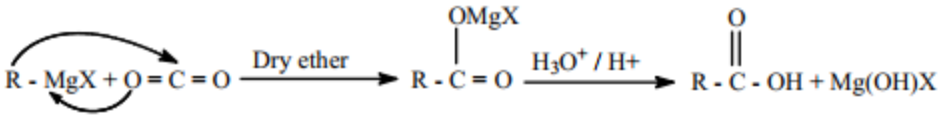
$$RCOOR^1 + HOH \xrightarrow{NaOH} RCOONa + R^1OH$$

V. Hydrolysis of Trihalides

All those compounds containing $-CCl_3$ group which is not directly attached to carbonyl group are hydrolysed with alkali to corresponding acid



VI. From R – Mg – X



VII. From Olefins (Koch reaction)

$$CH_2=CH_2+CO+H_2O(\text{steam})\xrightarrow[573-673K]{H_3PO_4}CH_3CH_2COOH$$

Physical properties :

1. Lower fatty acids upto C_{10} are colourless liquids, higher members are colourless waxy solids.
2. The first three members have a sharp pungent odour, the middle C_4 to C_9 have an odour of rancid butter, whereas higher members are odourless
3. Lower members are completely miscible with water and the solubility decreases with increasing molecular weight
4. B.P. of carboxylic acids increase regularly with increase in mol. wt.. BP of RCOOH > R-OH

Acidic Nature

- Among organic compounds, carboxylic acids are most acidic and ionize in aqueous solution

$$R-COOH+H_2O\rightleftharpoons RCOO^-+H_3O^+$$

$$K_a=\frac{[RCOO^-][H_3O^+]}{[RCOOH]};\qquad pK_a=-\log K_a$$

- The resulting carboxylate anion is stabilized by resonance, as negative charge is dispersed on both the oxygen atom
- Carboxylic acids are weaker than mineral acids, but they are stronger acids than alcohols, phenols and peroxy acids
- Electron withdrawing groups increase the acidity and electron donating groups decrease the acidity.
- All ortho - substituted acids are stronger than para and meta counterparts

Chemical properties

I Reactions involving cleavage of O-H bond

$$RCOOH+2Na\rightarrow 2RCOONa+H_2\uparrow$$

$$RCOOH+NaOH\rightarrow RCOONa+H_2O$$

$$RCOOH+NaHCO_3\rightarrow RCOONa+H_2O+CO_2$$

$$3RCOOH+Fe^{3+}+3AcO^-\rightarrow (RCOO)_3Fe+3AcOH$$

II Reactions involving cleavage of C–OH bond

a) Formation of anhydride

$$2CH_3COOH\xrightarrow[\Delta]{H_2SO_4/P_2O_5}(CH_3CO)_2O+H_2O$$

b) Esterification

$$CH_3COOH+C_2H_5OH\underset{}{\overset{\text{con.}H_2SO_4\text{ or HCl gas}}{\rightleftharpoons}}CH_3COOC_2H_5+H_2O$$

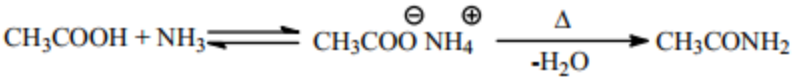
c) Reaction with PCl_5, PCl_3 and $SOCl_2$

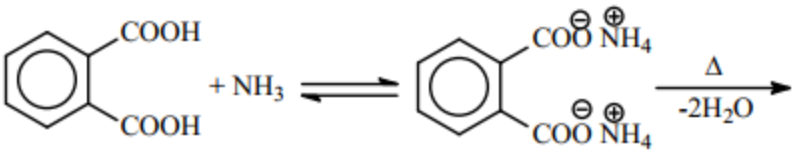
$$RCOOH + PCl_5 \rightarrow RCOCl + PCl_3 + HCl$$

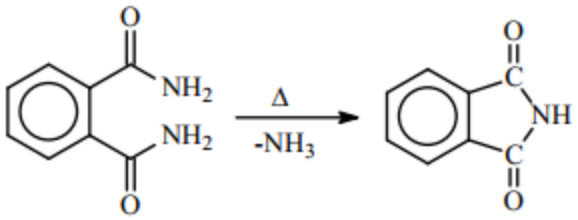
$$3RCOOH + PCl_3 \rightarrow 3RCOCl + H_3PO_3$$

$$RCOOH + SOCl_2 \rightarrow RCOCl + SO_2 \uparrow + HCl \uparrow$$

d) Reaction with NH_3







III. Reactions involving –COOH group

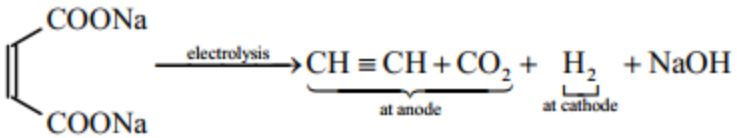
a) Reduction : R–COOH $\xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4/\text{ether or } B_2H_6} RCH_2OH$

b) De-carboxylation : $C_2H_5COONa \xrightarrow[\Delta]{NaOH+CaO} C_2H_6 + Na_2CO_3$

Acid first forms Na, K, or Ca carboxylate salts which loses CO_2 to form carbanion. More stable the carbanion formed, more readily the alkane is formed

c) Kolbe's electrolysis:

$$CH_3COONa \xrightarrow{\text{electrolysis}} \underbrace{CH_3 - CH_3 + CO_2}_{\text{at anode}} + \underbrace{H_2}_{\text{at cathode}} + NaOH$$



IV Substitution reaction

a) H.V.Z Reaction

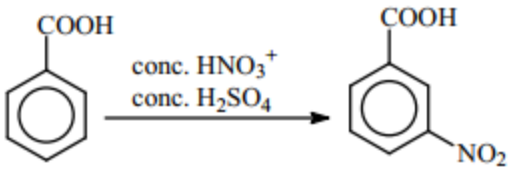
$$R - \underset{\alpha}{CH_2} - COOH \xrightarrow[(ii)\ H_2O]{(i)\ Cl_2 \text{ or } Br_2/\text{Red P}} R - \underset{Cl}{\underset{|}{CH}} - COOH \text{ or } R - \underset{Br}{\underset{|}{CH}} - COOH$$

Although monocarboxylic acid themselves are not readily halogenated, their acid chlorides and anhydrides are halogenated readily

b) Ring substitution

An aromatic acid undergoes S.E. reactions in which the –COOH group acts as a deactivating and meta directing group. It does not undergo F.C. reaction because the –COOH group is deactivating and the

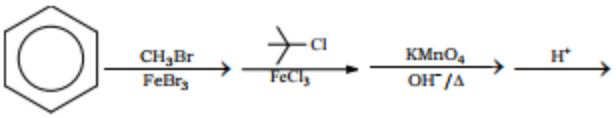
catalyst $AlCl_3$ gets bonded to the COOH group

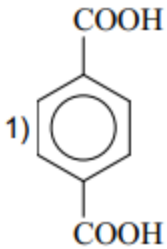


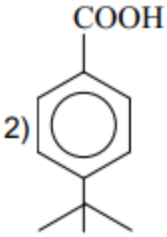
PART-I (JEE MAIN)

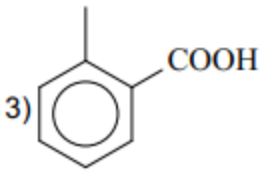
SECTION-I (Straight objective type questions)

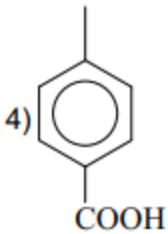
1. The final product in the following reaction sequence is



1) 

2) 

3) 

4) 

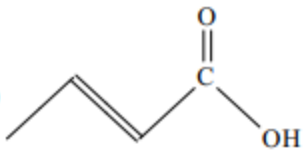
2. $CH_3-C\equiv C-H \xrightarrow{CH_3MgBr} CH_4 + A \xrightarrow[H_3O^+]{CO_2} B$

Product B in the above conversion is

1) $CH_3-\equiv-CH_2COOH$

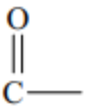
2) $CH_3-C\equiv C-MgBr$

3) $CH_3-\equiv-COOH$

4) 

3. R—CH_2—CH_2OH can be converted to R—CH_2CH_2COOH. The CORRECT sequence of reagents for the conversion is

1) PBr_3, KCN, H^+ 2) PBr_3, KCN, H_2 3) KCN, H^+ 4) HCN, PBr_3, H^+

4. Carboxylic acids do not give nucleophilic addition reaction eventhough they have  group. It is due to

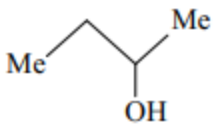
1) +I effect of R-group
2) –I effect of –COOH group
3) Hyperconjugation
4) Resonance

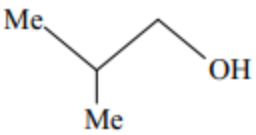
5. Carboxylic acid group can be easily detected by using

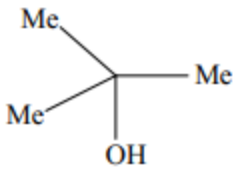
1) $NaHCO_3$ 2) 2,4-DNP 3) Iodoform test 4) Fehling's test

6. The decreasing order of rate of formation of ester for the following compounds with acetic acid in presence of H^+ is

i) 

ii) 

iii) 

iv) 

1) i > iii > ii > iv 2) i > ii > iii > iv 3) iv > ii> iii > i 4) iv > iii > ii > i

7. What are A and B in the following sequence of reactions

$$CH_3CH_2-COOH \xrightarrow[Br_2]{P} A \xrightarrow[(ii)H^+]{(i)\ alc.KOH} B$$

1) $CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-COOH,\ CH_2=CH-COOH$

2) $CH_3-CH_2-COBr,\ CH_2=CH-COOH$

3) $\underset{\displaystyle Br}{\underset{|}{CH_2}}-CH_2-COOH,\ CH_2=CH-COOH$

4) $CH_3-CH_2-COBr,\ CH_3-CH_2-COOH$

8. Assertion (A) : Compounds containing –CHO groups are easily oxidised with mild oxidising agents to corresponding carboxylic acids

Reason (R) : Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$

In the light of the above statements choose the correct option

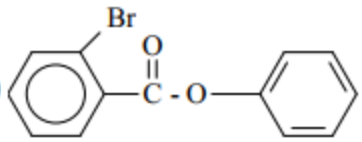
1) Both A and R are correct but R is not the correct explanation of A

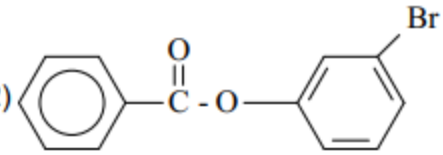
2) A is false but R is true

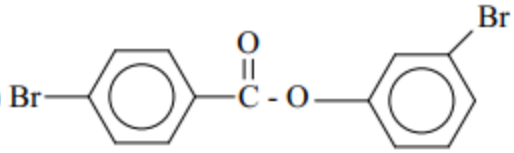
3) Both A and R are true and R is the correct explanation of A

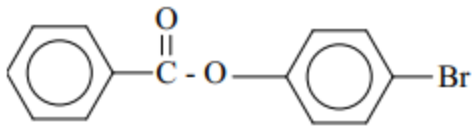
4) Both A and R are false

9. The major product obtained in the monobromination of phenyl benzoate is

1) 

2) 

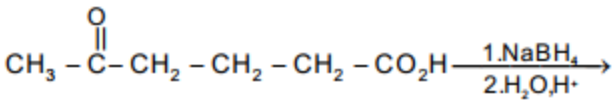
3) 

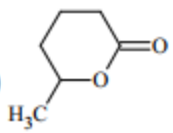
4) 

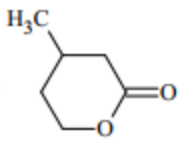
10. Benzoic acid when treated with bromine in presence of $FeBr_3$ forms

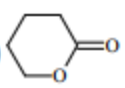
1) o-Bromobenzoic acid
2) Benzyl bromide
3) Benzoyl bromide
4) m-Bromobenzoic acid

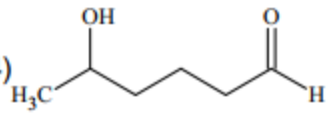
11. End product of the following conversion is



1) 

2) 

3) 

4) 

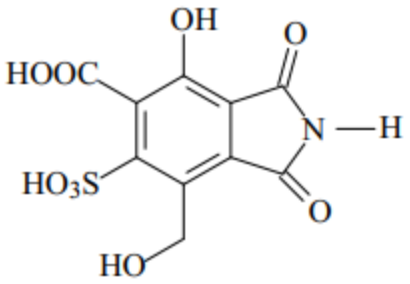
SECTION-II - Numerical Type Questions

12. Phthalic acid $\xrightarrow{NH_3}$ [X] $\xrightarrow{\text{strong heating}}$ Y

Total number of heteroatoms present in a molecule of Y is ——

13. Percentage of carbon in a carboxylic acid with molecular mass 146 is 49.3%. The number of carbon atoms present in the molecule is ——

14. The number of moles of NaOH that would react with one mole of the following compound is ———



15. The total number of compound (s) among the following that do(es) not undergo HVZ reaction is ——

1) Formic acid

2) Benzoic acid

3) 2,2-dimethyl propanoic acid

4) Ethanoic acid

5) 2-methyl propanoic acid

6) Salicylic acid

PART-II (JEE ADVANCED)

Section-III - Only one option correct type

16. Which of the following reactions is correct?

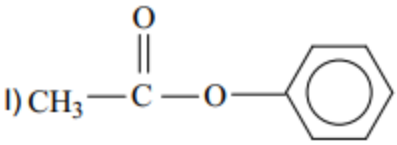
1) $CH_3-\overset{\overset{O}{\|}}{C}-{}^{18}OH + CH_3OH \xrightarrow{H^+} CH_3-\overset{\overset{O}{\|}}{C}-{}^{18}OCH_3 + H_2O$

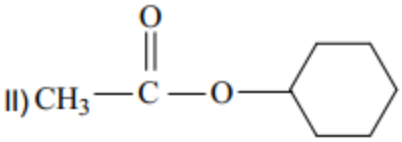
2) $CH_3-\overset{\overset{O}{\|}}{C}-{}^{18}OH + CH_3OH \xrightarrow{H^+} CH_3-\overset{\overset{O}{\|}}{C}-{}^{18}OCH_3 + H_2{}^{18}O$

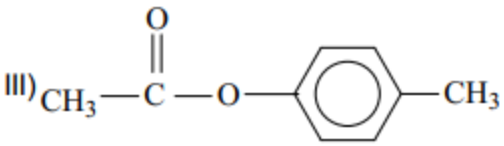
3) $CH_3-\overset{\overset{O}{\|}}{C}-{}^{18}OH + CH_3OH \xrightarrow{H^+} CH_3-\overset{\overset{O}{\|}}{C}-OCH_3 + H_2O$

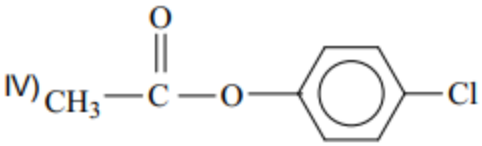
4) $CH_3-\overset{\overset{O}{\|}}{C}-OH + {}^{18}CH_3OH \xrightarrow{H^+} CH_3-\overset{\overset{O}{\|}}{C}-{}^{18}OCH_3 + H_2O$

17. List the following esters in the order of decreasing reactivity towards nucleophilic substitution reaction

I) 

II) 

III) 

IV) 

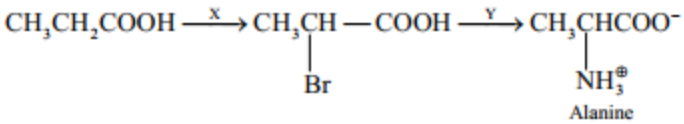
A) IV > I > III > II

B) IV > III > I > II

C) III > IV > I > II

D) II > I > III > IV

18. Consider the following reaction scheme:



Choose the correct set of reagents X and Y from the following

	X	Y
A)	Br_2	$NaNH_2$
B)	Br_2, P	NaOH
C)	Br_2, P	NH_3
D)	HBr	NH_3.

19. Which of the following dicarboxylic acids gives a cyclic anhydride on heating?

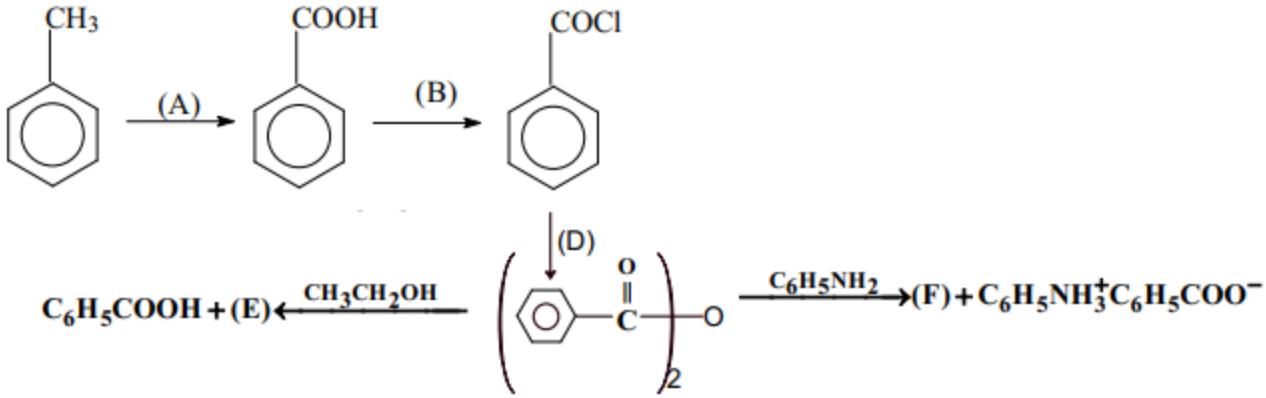
A) Oxalic acid

B) Succinic acid

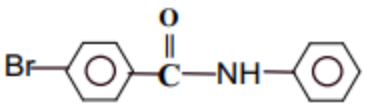
C) Adipic acid

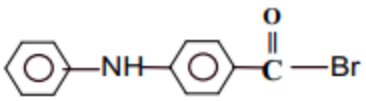
D) Malonic acid

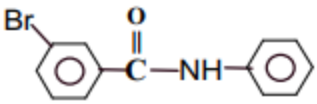
20. Consider the following reaction sequence.

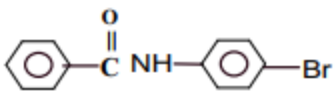


Compound (F) on treatment with Br_2/Fe mainly gives

A) 

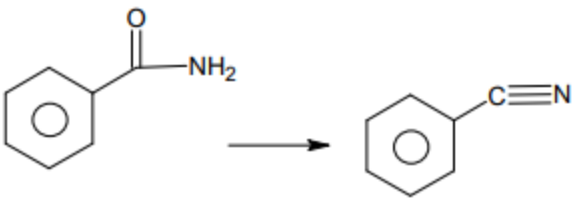
B) 

C) 

D) 

Section IV - One or more option correct type

21. The reagent (s) which can bring about the following transformation is/are



(A) P_2O_5 (B) $SOCl_2$ (C) $POCl_3$ (D) PCl_5

22. Which of the following compounds on hydrolysis yield(s) acetic acid?

A) CH_3CO_2MgX B) $CH_3C \equiv N$ C) CH_3COOCH_3 D) CH_3CH_2CN

23. When methanoic acid is treated with $NaH\overset{14}{C}O_3$, the gas(es) evolved is/are

A) H_2 B) ^{14}CO C) CO_2 D) $\overset{14}{C}O_2$

24. Which of the following is/are not correct for carboxylic acids?

A) Lower acids are largely soluble in water

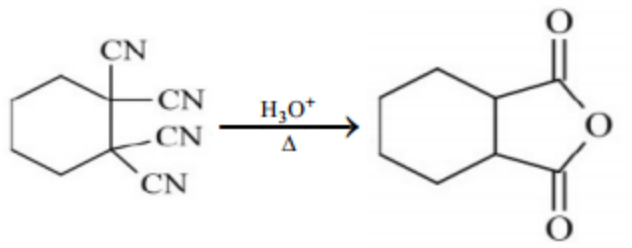
B) The hydrogen bonding in acids is weaker than that in alcohols

C) Carboxylic acids donot exist as dimer in the vapour phase

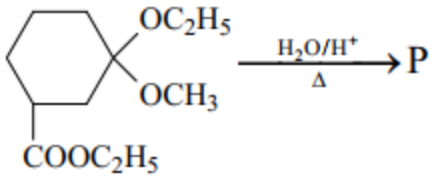
D) Benozic acid is insoluble in cold water where as soluble in benzene and ether

Section V - Numerical type questions

25. How many water molecules are eliminated in the following reaction ?



26. A mixture of $CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5$ and $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5$ is treated with C_2H_5ONa in ethanol. How many different condensation products (excluding stereoisomers) are formed in the reaction?

27. 

The number of alcohol molecules produced in the above reaction is ——

28. 59 g of an amide obtained from a carboxylic acid R–COOH, when heated with NaOH gave 17 g of NH_3. Find the total number of carbon atoms present in the parent acid (R-COOH)

Section-VI - Matrix match type

29. Match the following

Column I (Compound)	**Column II (Reactivity towards nucleophiles)**
(I) Acid chloride	(P) More reactive than aldehyde
(II) Acid anhydride	(Q) More reactive than carboxylic acid
(III) Ester	(R) More reactive than ketone
(IV) Acid amide	(S) More reactive than carboxylate

A) I - QRS, II - PQS, III - PQS, IV -QS

B) I-PQRS, II - QS, III- PQS, IV - S

C) I - PQRS, II - QS, III - QS, IV - S

D) I - QRS, II - PQS, III - QS, IV - QS

30. Match the following

Column-I **(Compound)**	**Column-II** **(Characteristic reaction)**
(I) HCOOH	(P) Effervescence of CO_2 with $NaHCO_3$
(II) CH_3COOH	(Q) Evolve hydrogen with Na
(III) Benzoic acid	(R) Decolourise Br_2 water
(IV) Cinnamic acid	(S) Give silver mirror with Tollens reagent

A) I - PQ, II - PQR, III - PQ, IV - PQ

B) I - PQS, II - PQR, III - PQR, IV - PQ

C) I - PQS, II - PQ, III - PQ, IV - PQR

D) I - PQS, II - PQ, III - PQR, IV - PQR