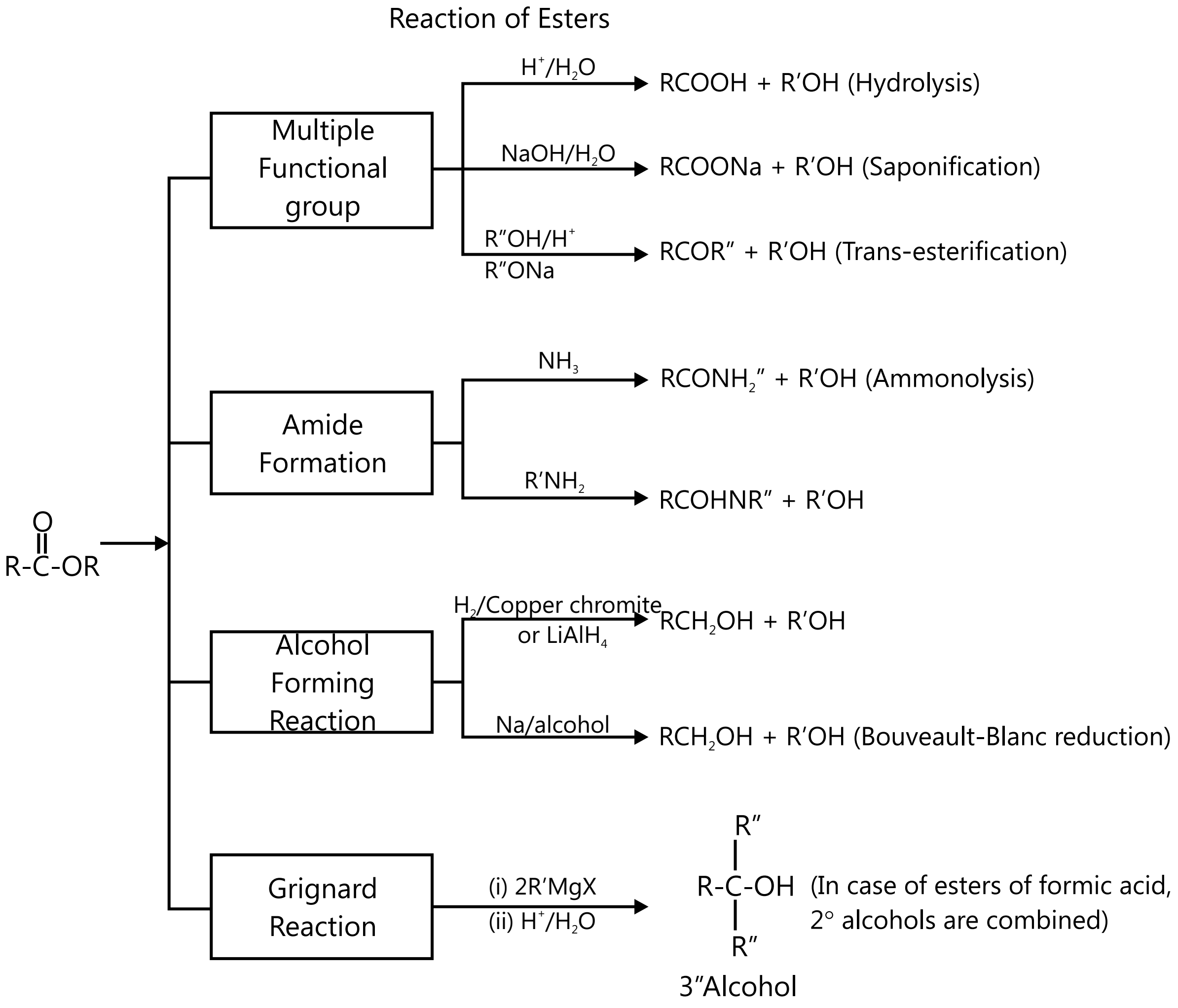
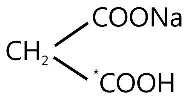
**(d) Summary of Reactions of Esters**

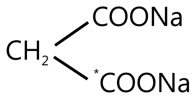


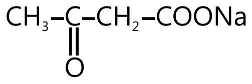
## Solved Examples

### JEE Main/Boards

**Example 1:** Select the correct statement about the following compounds I, II, II.


(I)


(II)


$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-COONa$

(III)

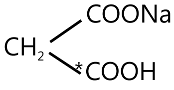
(A) (I) decarboxylates faster than (II) on heating.

(B) Only $^*CO_2$ is eliminated on heating of compound(I).

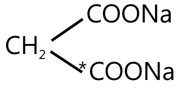
(C) Compound (I) eliminates a mixture of $CO_2$ and $^*CO_2$ on heating.

(D) The rate of decarboxylation of (II) is faster than (III).

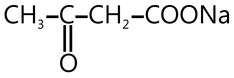
**Sol 1: (A)** Nature of functional group also has an influence on rate of decarboxylation. Presence of Electron Withdrawing Group-Increases its rate of decarboxylation.



(I)



(II)



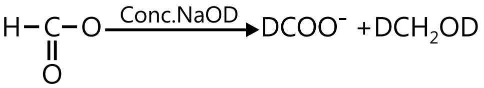
$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-COONa$

(III)

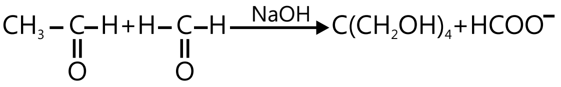
$CO_2$

rate of decarboxylation : III > I > II

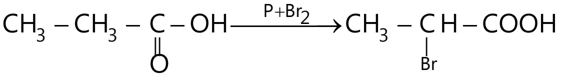
**Example 2:** Which of these represents correct reaction ?

(A) 

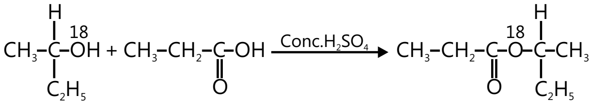
$H-\underset{\underset{O}{\|}}{C}-O\xrightarrow{Conc.NaOD}DCOO^- + DCH_2OD$

(B) 

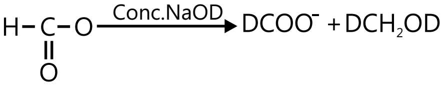
$CH_3-\underset{\underset{O}{\|}}{C}-H+H-\underset{\underset{O}{\|}}{C}-H\xrightarrow{NaOH}C(CH_2OH)_4+HCOO^-$

(C) 

$CH_3-CH_3-\underset{\underset{O}{\|}}{C}-OH\xrightarrow{P+Br_2}CH_3-\underset{\underset{Br}{|}}{C}H-COOH$

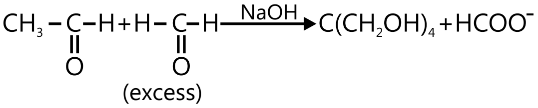
(D) 

$CH_3-\underset{\underset{C_2H_5}{|}}{\overset{\overset{H}{|}}{C}}-\overset{18}{O}H + CH_3-CH_2-\underset{\underset{O}{\|}}{C}-OH\xrightarrow{Conc.H_2SO_4}CH_3-CH_2-\underset{\underset{O}{\|}}{C}-\overset{18}{O}-\underset{\underset{C_2H_5}{|}}{\overset{\overset{H}{|}}{C}}-CH_3$

**Sol 2: (A, B, C, D)** 

$H-\underset{\underset{O}{\|}}{C}-O\xrightarrow{Conc.NaOD}DCOO^- + DCH_2OD$

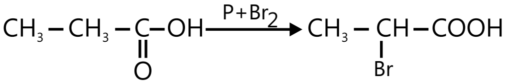
Cannizzaro reaction

(B) 

$CH_3-\underset{\underset{O}{\|}}{C}-H+H-\underset{\underset{O}{\|}}{C}-H\xrightarrow{NaOH}C(CH_2OH)_4+HCOO^-$

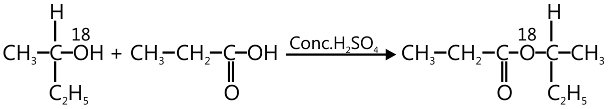
(excess)

Aldol + Cannizzaro reaction

(C) 

$CH_3-CH_3-\underset{\underset{O}{\|}}{C}-OH\xrightarrow{P+Br_2}CH_3-\underset{\underset{Br}{|}}{CH}-COOH$

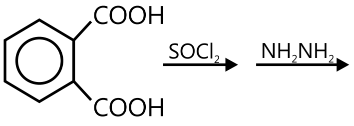
HVZ reaction

(D) 

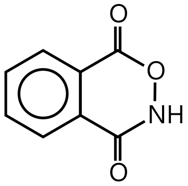
$CH_3-\underset{\underset{C_2H_5}{|}}{\overset{\overset{H}{|}}{C}}-\overset{18}{O}H + CH_3-CH_2-\underset{\underset{O}{\|}}{C}-OH\xrightarrow{Conc.H_2SO_4}CH_3-CH_2-\underset{\underset{O}{\|}}{C}-\overset{18}{O}-\underset{\underset{C_2H_5}{|}}{\overset{\overset{H}{|}}{C}}-CH_3$

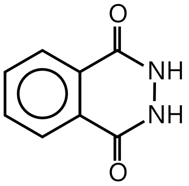
(Esterification reaction)

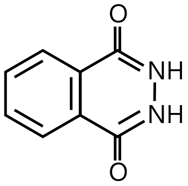
**Example 3:** Final product is :

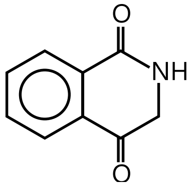


Phthalic acid

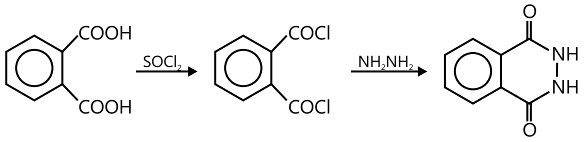
(A) 

(B) 

(C) 

(D) 

**Sol 3: (B)**



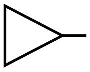
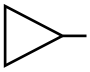
**Example 4:** Identify (A), (B), (C) and (D).

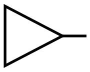
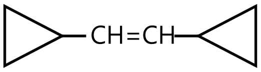
$C_3H_5Cl\ (A)\xrightarrow{Mg/dry\ ether}(B)\xrightarrow[(ii)H_2O/H^+]{(i)\ CO_2}(C)\xleftarrow{[O]}C_8H_{12}\ (D)$

Saturated

**Sol:** First step is preparation of gringnard reagent

Second is reaction of G. R. with $CO_2$ to form an acid

(A) =  Cl; (B) =  MgCl;

(C) =  COOH; (D) = 

**Example 5:** Give the reaction of preparation of propanoic acid from ethyl alcohol.

**Sol:** $CH_3-CH_2OH\xrightarrow[\text{(Haloalkane formation)}]{PCl_5}CH_3-CH_2-Cl$

$\xrightarrow[\text{Nucleophilic substitution}]{KCN}CH_3-CH_2-CN$

$\xrightarrow[\text{hydrolysis}]{H_2O/H^+}CH_3-CH_2-COOH$

Propanoic acid

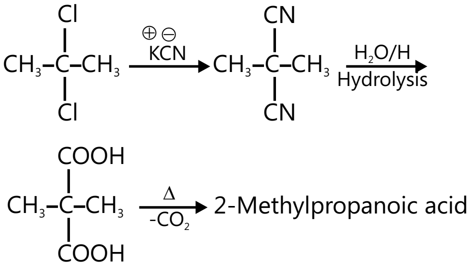
**Example 6:** Identify (A), (B) and (C).

$C_3H_6Cl_2\ (A)\xrightarrow{KCN}(B)\xrightarrow{H_2O/H^+}(C)\xrightarrow[-CO_2]{\Delta}$ :

2-Methylpropanoic acid

**Sol:** First step is Nocleophilic substitution ($CN^-$) followed by Hydrolysis. (Both Cl is replaced by CN)

It produces diacarboxylic acid which on mono decarboxylation produces 2-methyl propanoic acid.

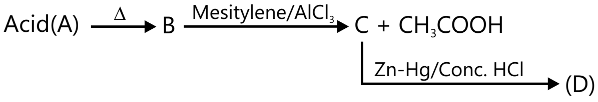


$$CH_3-\underset{Cl}{\overset{Cl}{C}}-CH_3 \xrightarrow{\overset{\oplus\ominus}{KCN}} CH_3-\underset{CN}{\overset{CN}{C}}-CH_3 \xrightarrow[\text{Hydrolysis}]{H_2O/H}$$

$$CH_3-\underset{COOH}{\overset{COOH}{C}}-CH_3 \xrightarrow[-CO_2]{\Delta} \text{2-Methylpropanoic acid}$$

## JEE Advanced/Boards

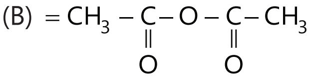
**Example 1:** Predict A, B, C, D and E.



$$\text{Acid(A)} \xrightarrow{\Delta} B \xrightarrow{\text{Mesitylene/AlCl}_3} C + CH_3COOH$$

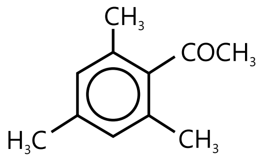
$$C \xrightarrow{\text{Zn-Hg/Conc. HCl}} (D)$$

**Sol 1:** (A) = $CH_3COOH$;

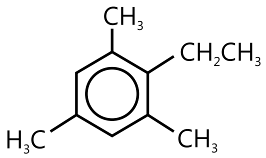


(B) $= CH_3-\underset{\overset{\|}{O}}{C}-O-\underset{\overset{\|}{O}}{C}-CH_3$

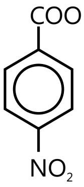
(c) =



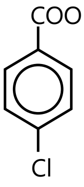
(D) =



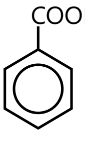
**Example 2:** Find the rate of soda-lime decarboxylation.



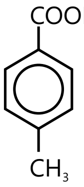
I



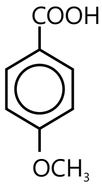
II



III



IV



V

**Sol 2:** Rate of soda-lime decarboxylation. I > II > III > IV > V

Presence of Electron withdrawing group Increases the rate of decarboxylation.

Presence of Eelectron donating group. decreases the rate of decarboxylation.

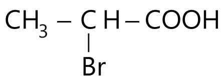
$-NO_2$, $-Cl^-$ Electron withdrawing group thus rate of decarboxylation increases

$-CH_3$, $-OCH_3$ Electron donating group and hence rate decreases.

**Example 3:** Identify (A), (B) and (C).

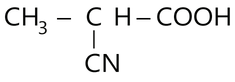
$$CH_3-CH_2-COOH \xrightarrow{Br_2(1\ eqv)/P} (A) \xrightarrow{KCN} (B) \xrightarrow{H_2O/H'/\Delta} (C)$$

**Sol 3:** (A)



$CH_3-\underset{Br}{CH}-COOH$

(B)



$CH_3-\underset{CN}{CH}-COOH$

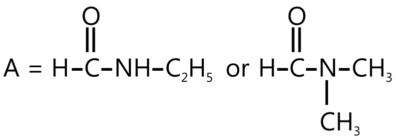
(C) $CH_3-CH(COOH)_2$

**Example 4:** Write the structures of (A) $C_3H_7NO$ which on acid hydrolysis gives acid (B) and amine (C). Acid (B) gives (+)ve silver-mirror test.

**Sol:** Since it gives positive silver mirror Test, It has to be an aldehyde (-CHO)

$C_3H_7NO-CHO=C_2H_6N$,

Now $C_2H_6N$ can be either $(CH_3)_2N$ or $CH_3CH_2$-NH group. Thus A can be.

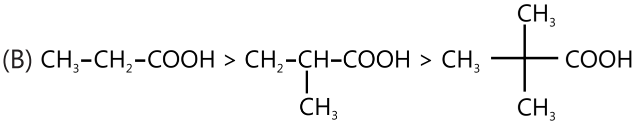


$A = H-\overset{O}{\overset{\|}{C}}-NH-C_2H_5$ or $H-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{N}-CH_3$

**Example 5:** Which are correct against property mentioned?

(A) $CH_3COCl > (CH_3CO)_2O > CH_3COOEt > CH_3CONH_2$

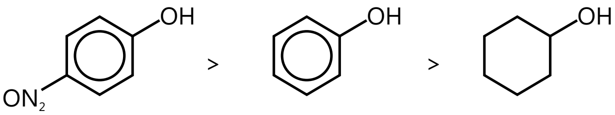
(Rate of hydrolysis)



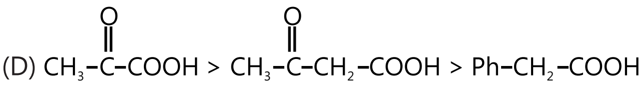
(B) $CH_3-CH_2-COOH > CH_2-\underset{CH_3}{CH}-COOH > CH_3-\underset{CH_3}{\overset{CH_3}{C}}-COOH$

(Rate of esterification)

(C)



(Rate of esterification)

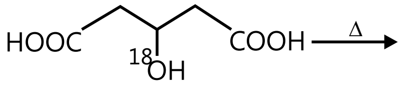
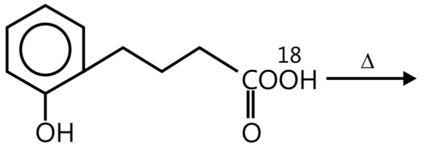
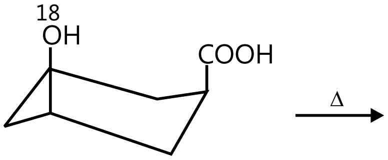
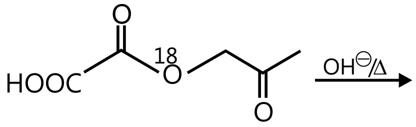


(D) $CH_3-\overset{O}{\overset{\|}{C}}-COOH > CH_3-\overset{O}{\overset{\|}{C}}-CH_2-COOH > Ph-CH_2-COOH$

(Rate of decarboxylation)

**Sol 5: (A, B)** Self explanatory

**Example 6:** Match the product of column II with the reaction of column I.

| Column I | | Column II | |
|---|---|---|---|
| (A) |  | (p) | Ester with $O^{18}$ |
| (B) |  | (q) | A β-diketone with $-^{18}OH$ group |
| (C) |  | (r) | A cyclic anhydride with $-^{18}OH$ group |
| (D) |  | (s) | A cyclic ester without $O^{18}$ |

**Sol:** A → r; B → s; C → p; D → q

Self explanatory

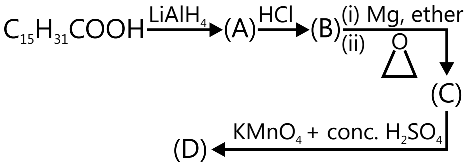
## JEE Main/Boards

## Exercise 1

**Q.1** Two isomeric carboxylic acids H and I, $C_9H_8O_2$, react with $H_2$/Pd giving compounds $C_9H_{10}O_2$. H gives a resolvable product and I gives a non-resolvable product. Both isomers can be oxidized to $C_6H_5COOH$.

Give the structure of H and I.

**Q.2** Identify the products (A), (B), (C) and (D) in the following sequence:



**Q.3** A neutral liquid (Y) has the molecular formula $C_6H_{12}O_6$. On hydrolysis it yields an acid (A) and an alcohol (B). Compound (A) has a neutralization equivalent of 60. Alcohol (B) is not oxidized by acidified $KMnO_4$, but gives cloudiness immediately with Lucas reagent. What are (Y), (A) and (B) ?

**Q.4** Esterification does not take place in the presence of ethyl alcohol and excess of concentrated $H_2SO_4$ at 170°C. Explain.

**Q.5** Why does carboxylic acid functions as bases though weak ones?

**Q.6** Which ketone of the formula $C_5H_{10}O$ will yield an acid on halo form reaction?

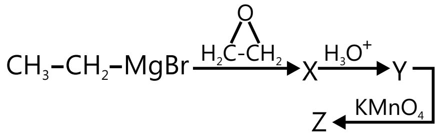
**Q.7** Highly branched carboxylic acids are less acidic than unbranched acids. Why?

**Q.8** A carboxylic acid does not form an oxime or phenyl hydrazone. Why?

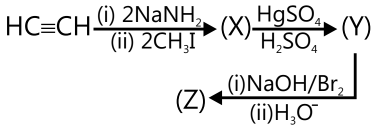
**Q.9** Formic acid reduce Tollen's reagent. Why?

**Q.10** The $K_2$ for fumaric acid is greater than maleic acid. Why.

**Q.11** Identify the final product in the following sequence of reaction.



**Q.12** What is (Z) in the following sequence of reactions ?



**Q.13** Acetic acid has a molecular weight of 120 in benzene solution why ?

**Q.14** Place the following in the correct order of acidity

(i) CH≡C–COOH; (ii) $CH_2$=CH–COOH;

(iii) $CH_3CH_2COOH$

**Q.15** Phenol is a weaker acid than acetic acid why?

**Q.16** Which acid derivative show most vigorous alkaline hydrolysis ?

**Q.17** 59 g of amide obtained from the carboxylic acid RCOOH, on heating with alkali gave 17g of ammonia. What is the formula of acid ?

**Q.18** Which carboxylic acid (X) of equivalent mass of 52g / eq loses $CO_2$ when heated to give an acid (Y) of equivalent mass of 60g/eq.

**Q.19** Which of the reagent reacts with $C_6H_5CH_2CONH_2$ to form $C_6H_5CH_2CN$.

**Q.20** Consider the following ester -

(i) $MeCH_2COOH$ (ii) $Me_2CHCOOH$

(iii) $Me_3CCOOH$ (iv) $Et_3CCOOH$

Correct order of the rate of esterification

**Q.21** An organic compound (A) on treatment with ethyl alcohol gives a carboxylic acid (B) and compound (C). Hydrolysis of (C) under acidic conditions gives (B) and (D). Oxidation of (D) with $KMnO_4$ also gives (B). (B) on heating with $Ca(OH)_2$ gives (E) (Molecular formula $C_3H_6O$) (E) does not gives Tollen's test and does not reduce Fehling solution but forms 2, 4-dinitrophenylhydrazone. Identify (A) to (E).

**Q.22** Two mole of an ester (A) are condensed in presence of sodium ethoxide to give a β-ketoester (B) and ethanol. On heating in an acidic solution(B) gives ethanol and β-ketoacid(C). On decarboxylation (C) gives 3-pentanone. Identify (A), (B) and (C) with reactions.

**Q.23** Compound(A)($C_6H_{12}O_2$) on reaction with $LiAlH_4$ yields two compounds (B) and (C). The compound (B) on oxidation gave (D) 2 moles of (D) on treatment with alkali (aqueous) and subsequent heating furnished (E). The later on catalytic hydrogenation gave (C). The compound (D) was oxidized further to give (F) which was found to be a monobasic acid (m.wt.60.0). Deduce structures of (A) to (E).

**Q.24** Compound (A) $C_5H_8O_2$ liberated $CO_2$ on reaction with sodium bicarbonate. It exists in two forms neither of which is optically active. It yielded compound (B). $C_5H_{10}O_2$ on hydrogenation. Compound (B) can be separated into enantimorphs. Write structures of (A) and (B).

**Q.25** The sodium salt of a carboxylic acid, (A) was produced by passing a gas (B) into aqueous solution of caustic alkali at an elevated temperature and pressure (A) on heating in presence of sodium hydroxide followed by treatment with sulphuric acid gave a dibasic acid (C). A sample of 0.4g of (C) on combustion gave 0.08 g of $H_2O$ and 0.39 g of $CO_2$. The silver salt of the acid, weighing 1.0 g, on ignition yielded 0.71 g of Ag as residue. Identify (A), (B) and (C).

**Q.26** An organic compound (A) on treatment with acetic acid in presence of sulphuric acid produces an ester (B). (A) on mild oxidation gives (C). (C) with 50% KOH followed by acidification with dilute HCl generates (A) and (D). (D) with $PCl_5$ followed by reaction with ammonia gives (E). (E) on dehydration produces hydrocyanic acid. Identify (A) to (E).

**Q.27** Acetophenone on reaction with hydroxylamine-hydrochloride can produce two isomeric oximes. Write structures of the oximes.

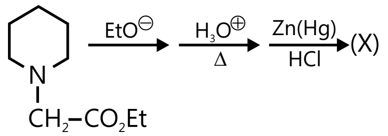
**Q.28** An acidic compound (A), $C_4H_8O$ loses its optical activity on strong heating yielding (B). $C_4H_6O_2$ which reacts readily with $KMnO_4$. (B) forms a derivative (C) with $SOCl_2$, which on reaction with $(CH_3)_2NH$ gives (D). The compound (A) on oxidation with dilute chromic acid gives an unstable compound (E) which decarboxylates readily to give (F), $C_3H_6O$. The compound (F) gives a hydrocarbon (G) on treatment with amalgamated Zn and HCl. Give structures of (A) to (G) with proper reasoning.

**Q.29** An organic acid (A), $C_5H_{10}O_2$ reacts with $Br_2$ in the presence of phosphorus to give (B). Compound (B) contains an asymmetric carbon atom and yields (C) on dehydrobromination. Compound (C) does not show geometric Isomerism and on decarboxylation gives an alkene (D) which on ozonolysis gives (E) and (F). Compound (E) gives a positive Schiff's test but (F) does not. Give structures of (A) to (F) with reasons.

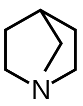
**Q.30** An liquid (X) having molecular formula $C_6H_{12}O_2$ is hydrolysed with water in presence of an acid to give a carboxylic acid (Y) and an alcohol (Z). Oxidation of (Z) with chromic acid gives (Y). What are (X), (Y) and (Z) ?

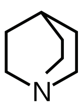
## Exercise 2

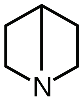
### Single Correct Choice Type

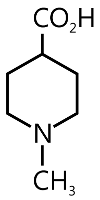
**Q.1** 

Product (X) of above reaction is :

(A) 

(B) 

(C) 

(D) 

**Q.2** Correct order of reactivity of following acid derivatives is

(I) MeCOCl

(II) $MeCON_3$

(III) MeCOOCOMe

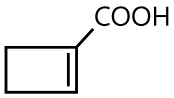
(A) I > II > III

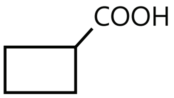
(B) II > I > III

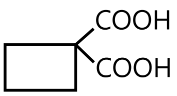
(C) I > III > II

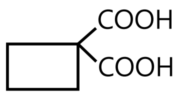
(D) II > III > I

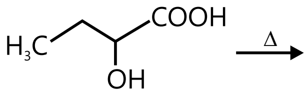
**Q.3** $CH_2(COOEt)_2 + (CH_2)_3 \xrightarrow[EtOH]{NaOEt} I \xrightarrow{H_3O^+} II$ is :

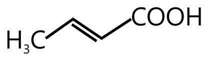
(A) 

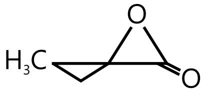
(B) 

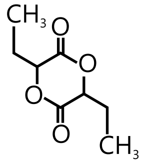
(C) 

(D) 

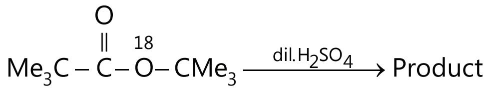
**Q.4**  X, X will be

(A) 

(B) 

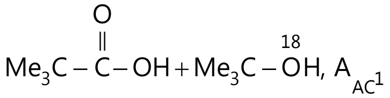
(C) 

(D) None

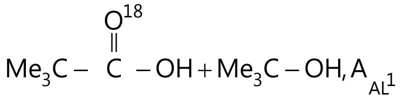
**Q.5** 

$\mathrm{Me_3C-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{18}{O}-CMe_3 \xrightarrow{dil.H_2SO_4}}$ Product

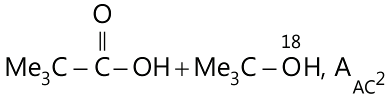
of this reaction and the mechanism is :

(A) 

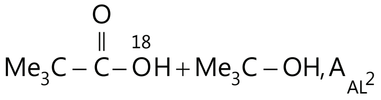
$\mathrm{Me_3C-\overset{\overset{\displaystyle O}{\|}}{C}-OH+Me_3C-\overset{18}{O}H,\ A_{AC}1}$

(B) 

$\mathrm{Me_3C-\overset{\overset{\displaystyle O^{18}}{\|}}{C}-OH+Me_3C-OH, A_{AL}1}$

(C) 

$\mathrm{Me_3C-\overset{\overset{\displaystyle O}{\|}}{C}-OH+Me_3C-\overset{18}{O}H,\ A_{AC}2}$

(D) 

$\mathrm{Me_3C-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{18}{O}H+Me_3C-OH, A_{AL}2}$

**Q.6** Guess the product

$CH_3CH_2CONH_2 \xrightarrow[\Delta]{PCl_5}$ ?

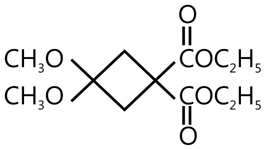
(A) $CH_3CH_2$–CN

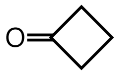
(B) $CH_3CH_2COCl$

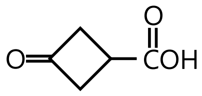
(C) $CH_3CCl_2CONH_2$

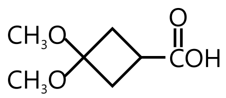
(D) $CH_3CH_2CONHCl$

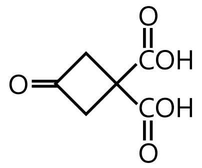
**Q.7** End product due to hydrolysis of (A) and subsequent heating is :

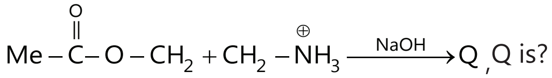


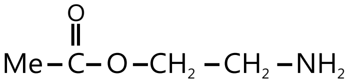
(A) 

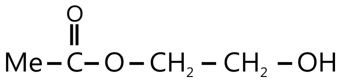
(B) 

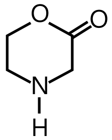
(C) 

(D) 

**Q.8** 
$\mathrm{Me}-\overset{O}{\overset{\|}{C}}-O-CH_2+CH_2-\overset{\oplus}{N}H_3 \xrightarrow{NaOH} Q$ ,Q is?

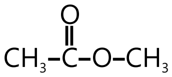
(A) 
$\mathrm{Me}-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-NH_2$

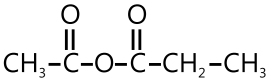
(B) 
$\mathrm{Me}-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-OH$

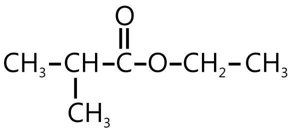
(C) 

(D) MeCOONa + $HOCH_2CH_2NH_2$

**Q.9** Which of the following give two alcohols when it reacts with $LiAlH_4$.

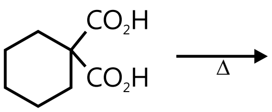
(A) 
$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$

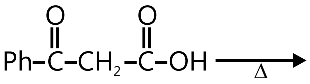
(B) 
$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

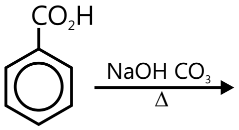
(C) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$

(D) All

**Q.10** In which of the following reaction $CO_2$ gas will be evolved.

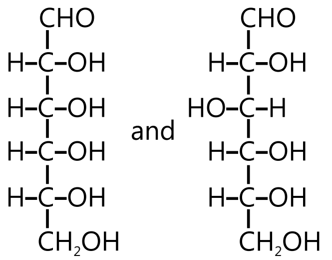
(A) 

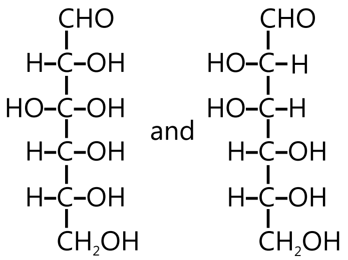
(B) 
$Ph-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\Delta]{}$

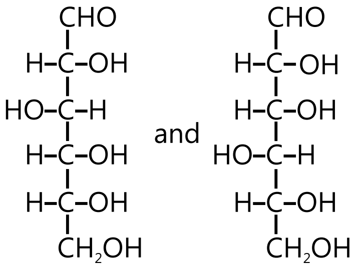
(C) 

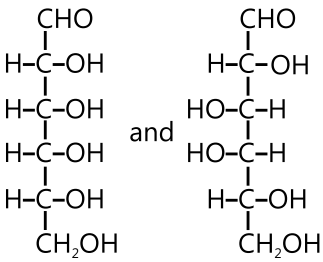
(D) All

**Q.11** Which of the following pair will form same osazone when it reacts phenyl hydrazine

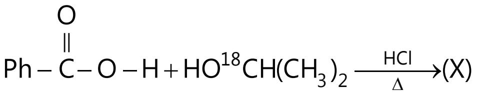
(A) 
D-allose D-glucose

(B) 
D-glucose D-mannose

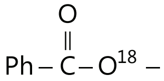
(C) 
D-glucose D-gulose

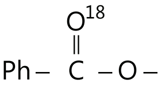
(D) 
D-allose D-glucose

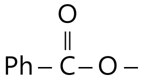
**Q.12**


$Ph-\overset{O}{\overset{\|}{C}}-O-H+HO^{18}CH(CH_3)_2 \xrightarrow[\Delta]{HCl} (X)$

Major product (X) is :

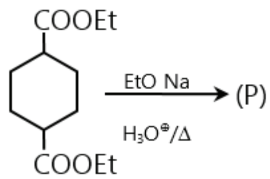
(A) 
$Ph-\overset{O}{\overset{\|}{C}}-O^{18}-$

(B) 
$Ph-\overset{O^{18}}{\overset{\|}{C}}-O-$

(C) 
$Ph-\overset{O}{\overset{\|}{C}}-O-$

(D) Ph–O–

**Q.13**



Select **incorrect** statement

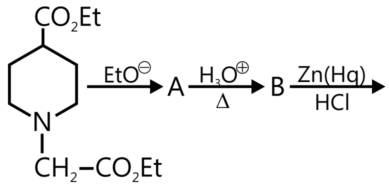
(A) P can turn blue litmus red

(B) P can not give effervescence of $CO_2$ with $NaOH_3$.

(C) It is Dieckmann condensation

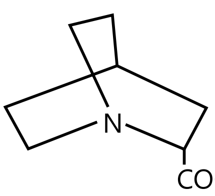
(D) Product is a bicylo compound

**Q.14**

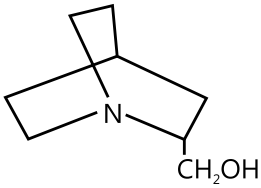


C, C is C is

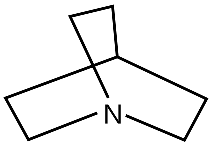
(A)



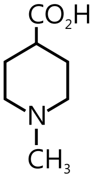
(B)



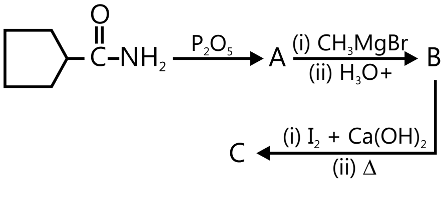
(C)



(D)

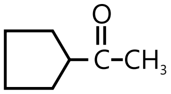


**Q.15**

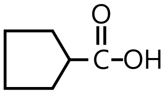


Product is:

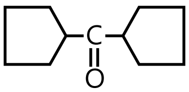
(A)



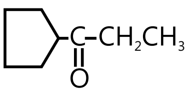
(B)



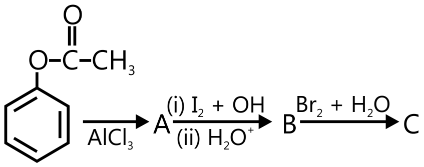
(C)



(D)



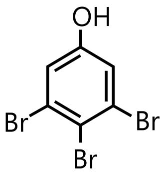
**Q.16**



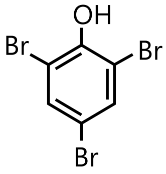
'C' form white precipitate compound 'C' is:

(A)

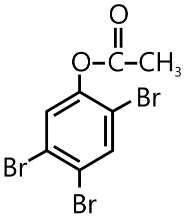
(B)



(C)



(D)



**Q.17** Which of the following esters cannot undergo self Claisen condensation

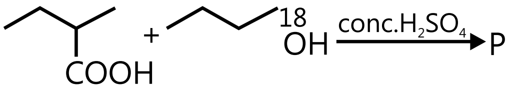
(A) $CH_3CH_2CH_2CH_2CO_2C_2H_5$

(B) $C_6H_5CO_2C_2H_5$

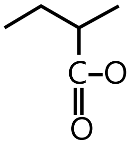
(C) $C_6H_5CH_2CO_2C_2H_5$

(D) $CH_3CH_2CO_2C_2H_5$

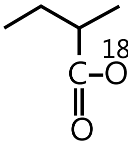
**Q.18**



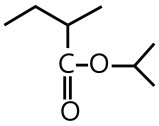
(A)



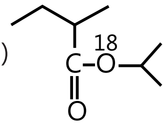
(B)



(C)



(D)



**Q.19** Method to distinguish $RNH_2$ & $R_2NH$

(A) $NaNO_2$/HCl

(B) Hoffmann's mustard oil reaction

(C) Hinsberg test

(D) All of the above

## Previous Years' Questions

**Q.1** When propionic acid is treated with aqueous sodium bicarbonate, $CO_2$ is liberated. The C of $CO_2$ comes from ***(1999)***

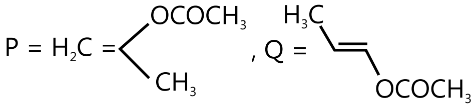
(A) Methyl group (B) Carboxylic acid group

(C) Methylene group (D) Bicarbonate group

**Q.2** Benzoyl chloride is prepared from benzoic acid by ***(2000)***

(A) $Cl_2, h\nu$ (B) $SO_2Cl_2$ (C) $SOCl_2$ (D) $Cl_2, H_2O$

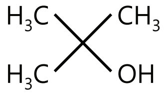
**Q.3** The product of acid hydrolysis of P and Q can be distinguished by ***(2003)***

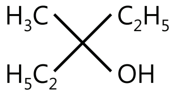


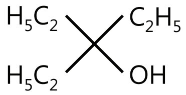
(A) Lucas reagent (B) 2,4-DNP

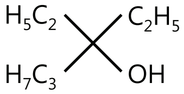
(C) Fehling's solution (D) $NaHSO_3$

**Q.4** Ethyl ester $\xrightarrow[\text{(excess)}]{CH_3MgBr}$ P, the product 'P' will be ***(2003)***

(A)


(B)


(C)


(D)


**Q.5** An enantiomericaily pure acid is treated with racemic mixture of an alcohol having one chiral carbon. The ester formed will be ***(2003)***

(A) Optically active mixture

(B) Pure enantiomer

(C) Meso compound

(D) Racemic mixture

**Q.6** Benzamide on treatment with $POCl_3$ gives : ***(2004)***

(A) Aniline (B) Benzonitrile

(C) Chlorobenzene (D) Benzyl amine

**Q.7 Statement-I:** Acetic acid does not undergo haloform reaction.

**Statement-II:** Acetic acid has no alpha hydrogen. ***(1998)***

**Q.8 Statement-I:** p-hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.

**Statement-II:** o-hydroxybenzoic acid has intramolecular hydrogen bonding. ***(2007)***

**Q.9** Hydrolysis of an ester in presence of a dilute acid is known as saponification. ***(1983)***

**Q.10** The boiling point of propanoic acid is less than that of n-butyl alcohol, an alcohol of comparable molecular weight. ***(1991)***

**Q.11** 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: ***(2009)***

(A) $CH_3OH$ (B) HCHO

(C) $CH_3COCH_3$ (D) $CH_3COOH$

**Q.12** Sodium ethoxide has reacted with ethanoyl chloride. The compound that is produced in the above reaction is: ***(2011)***

(A) 2-Butanone (B) Ethyl chloride

(C) Ethyl ethanoate (D) Diethyl ether

**Q.13** The strongest acid amongst the following compounds is: ***(2011)***

(A) HCOOH

(B) $CH_3CH_2CH(Cl)CO_2H$

(C) $ClCH_2CH_2CH_2COOH$

(D) $CH_3COOH$

**Q.14** Which of the following reagents may be used to distinguish between phenol and benzoic acid? ***(2011)***

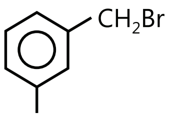
(A) Tollen's reagent (B) Molisch reagent

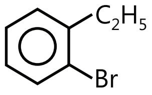
(C) Neutral $FeCl_3$ (D) Aqueous NaOH

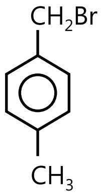
**Q.15** A compound with molecular mass 180 is acylated with $CH_3COCl$ to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is: ***(2013)***

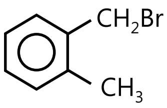
(A) 2 (B) 5 (C) 4 (D) 6

**Q.16** Compound (A), $C_8H_9Br$, gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A). ***(2013)***

(A) 

(B) 

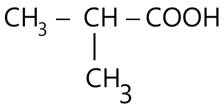
(C) 

(D) 

**Q.17** An organic compound A upon reacting with $NH_3$ gives B. On heating B gives C. C in presence of KOH reacts with $Br_2$ to given $CH_3CH_2NH_2$. A is: ***(2013)***

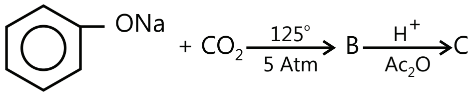
(A) $CH_3COOH$

(B) $CH_3CH_2CH_2COOH$

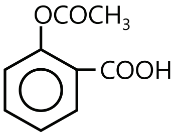
(C) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$

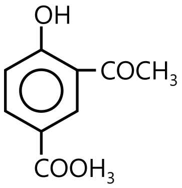
(D) $CH_3CH_2COOH$

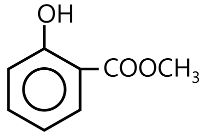
**Q.18** Sodium phenoxide when heated with $CO_2$ under pressure at 125°C yields a product which on acetylation produces C.

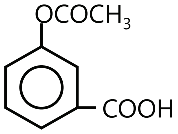


The major product C would be ***(2014)***

(A) 

(B) 

(C) 

(D) 

**Q.19** In the reaction,

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

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

(A) Acetaldehyde

(B) Acetylene

(C) Ethylene

(D) Acetyl chloride

**Q.20** In the following sequence of reactions:

$$\text{Toluene} \xrightarrow{KMnO_4} A \xrightarrow{SICl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C$$

the product C is: ***(2015)***

(A) $C_6H_5COOH$

(B) (B) $C_6H_5CH_3$

(C) (C) $C_6H_5CH_2OH$

(D) $C_6H_5CHO$

**Q.21** In the Hofmann bromamide degradation reaction, the number of moles of NaOH and $Br_2$ used per mole of amine produced are: ***(2016)***

(A) Four moles of NaOH and two moles of $Br_2$

(B) Two moles of NaOH and two moles of $Br_2$

(C) Four moles of NaOH and one mole of $Br_2$

(D) One mole of NaOH and one mole of $Br_2$

## JEE Advanced/Boards

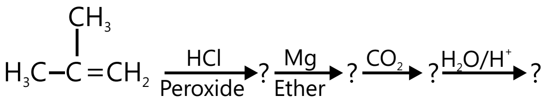
### Exercise 1

**Q.1** (i) Give the structures of the four optically-active isomers of $C_4H_8O_3$ (D through G) that evolve $CO_2$ with aq. $NaHCO_3$.

(ii) Find the structure of (D), the isomer that reacts with $LiAlH_4$ to give an achiral product.

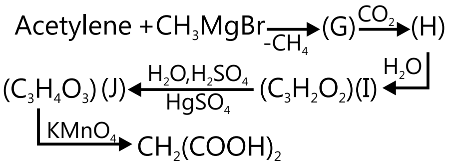
(iii) Give chemical reactions to distinguish among (E), (F) and (G).

**Q.2** Complete the following equation:



$$H_3C-\overset{\overset{\large CH_3}{|}}{C}=CH_2 \xrightarrow[\text{Peroxide}]{HCl} ? \xrightarrow[\text{Ether}]{Mg} ? \xrightarrow{CO_2} ? \xrightarrow{H_2O/H^+} ?$$

**Q.3** Give structures of compounds:



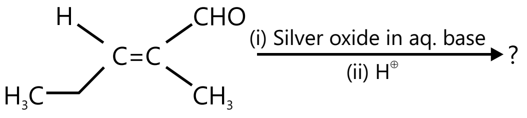
**Q.4** An ester $C_6H_{12}O_2$ was hydrolysed with water an acid (A), and an alcohol (B), were obtained. Oxidation of (B) with chromic acid produced A. What is the structure of the original ester? Write equations for all the reactions.

**Q.5** Complete the following equation:

$$RCO_2H \xrightarrow{SOCl_2} ? \xrightarrow{NaN_2} ? \xrightarrow[\text{(inert solvent)}]{D} ? \xrightarrow{\text{Hydrolysis}} ?$$

**Q.6** Acid halides of formic acid are unstable. Why?

**Q.7** What is the product of the following reaction?



2-Methyl-2-pentenal

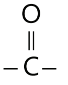
**Q.8** An unsaturated acid (A) of molecular formula $C_5H_6O_4$ eliminates $CO_2$ easily and gives another unsaturated acid (B) of formula $C_4H_6O_2$. By saturation with $H_2$/Pt (B) gives butanoic acid. Neither (A) nor (B) shows cis-trans isomerism. What are (A) and (B)?

**Q.9** An organic compound 'A' on treatment with ethyl alcohol gives a carboxylic acid 'B' and compound 'C' Hydrolysis of 'C' under acidic conditions gives 'B' and 'D' Oxidation of 'D' with $KMnO_4$ also gives 'B' . 'B' on heating with $Ca(OH)_2$ gives 'E'(molecular formula $C_3H_6O$). 'E' doesnot give Tollen's test and does not reduce Fehling's solution but forms a 2,4-dinitrophenyl hydrazine. Identify 'A. B' C' 'D' and 'E'.

**Q.10** Two moles of an ester (A) are condensed in the presence of sodium ethoxide to give a β–keto ester (B) and ethanol. On heating in an acidic solution (B) gives ethanol and β–keto acid (C). On decarboxylation (C) gives 3–pentanone. Identify (A), (B) and (C) with proper reasoning. Name the reaction involved in the conversion of (A) to (B).

**Q.11** An alkali salt of palmitic acid is known as?

**Q.12** Acid do not react with sodium bisulphite though they have



$-\overset{\overset{O}{\|}}{C}-$ group. Why ?

**Q.13** In the reaction sequence

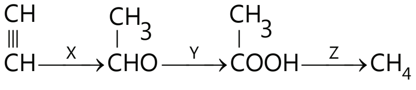
$$X \xrightarrow{Ca(OH)_2} Y \xrightarrow[\text{distillation}]{\text{Dry}} \text{Acetone} \xrightarrow[H_2SO_4]{\text{Conc.}} Z$$

X, Y and Z are ?

**Q.14** $CH_3CH_2COOH \xrightarrow[SeO_2]{[O]} X$, Product X is–

**Q.15** Which of the reagent attack only the carbonyl group of a fatty acid?

**Q.16** In the sequence



$$\underset{CH}{\overset{CH}{|||}} \xrightarrow{X} \overset{\overset{CH_3}{|}}{C}HO \xrightarrow{Y} \overset{\overset{CH_3}{|}}{C}OOH \xrightarrow{Z} CH_4$$

The reagent X, Y and Z are:

**Q.17** In the reaction sequence

$$X \xrightarrow{H_3O^{\oplus}} Y \xrightarrow[\Delta]{NH_3} Z \xrightarrow[KOH]{Br_2} CH_3NH_2$$

X, Y, and Z are?

**Q.18** An acid X react with $PCl_5$ to form a compound (Y). X also react with NaOH to form a compound (Z). Both Y and Z react together and from (E), E react with a reagent (F) to give back compound (Y) what are X, F , Z,E and F?

**Q.19** How will you synthesise?

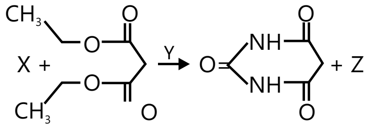
(i) Acetyl chloride from methyl chloride

(ii) Acetamide from ethyl alcohol

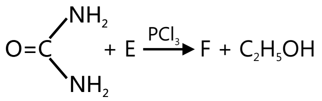
(iii) Ethyl acetate from acetic acid

**Q.20** Complete the following reaction?

(i)

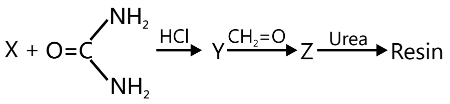


(ii)



$O{=}C(NH_2)_2 + E \xrightarrow{PCl_3} F + C_2H_5OH$

(iii)

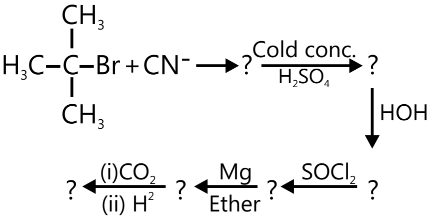


$X + O{=}C(NH_2)_2 \xrightarrow{HCl} Y \xrightarrow{CH_2{=}O} Z \xrightarrow{Urea} \text{Resin}$

**Q.21** Complete the following equations:

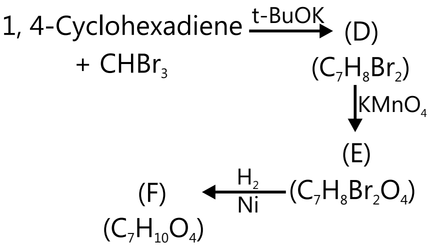
(i) $CH_3CH_2CH_2CH_2Br \xrightarrow{CN-} ? \xrightarrow{H_2O/H^+} ?$

(ii)



$H_3C{-}C(CH_3)_2{-}Br + CN^- \longrightarrow ? \xrightarrow[H_2SO_4]{\text{Cold conc.}} ? \xrightarrow{HOH} ? \xrightarrow{SOCl_2} ? \xrightarrow[\text{Ether}]{Mg} ? \xrightarrow[\text{(ii) }H^2]{\text{(i)}CO_2} ?$

**Q.22** Identify the compounds:



$\text{1, 4-Cyclohexadiene} + CHBr_3 \xrightarrow{\text{t-BuOK}} \underset{(C_7H_8Br_2)}{(D)} \xrightarrow{KMnO_4} \underset{(C_7H_8Br_2O_4)}{(E)} \xrightarrow[Ni]{H_2} \underset{(C_7H_{10}O_4)}{(F)}$

**Q.23** Compound (A) $C_5H_8O_2$ liberated carbon dioxide on reaction with sodium bicarbonate. It exists in two forms neither of which is optically active. It yields compound (B) $C_5H_{10}O_2$ on hydrogenation. Compound (B) can be separated into two enantiomorphs. Write the structural formulae of (A) and (B) giving reason.

**Q.24** An acidic compound (A), $C_4H_8O_3$ loses its optical activity on strong heating yielding (B), $C_4H_6O$ which reacts readily with $KMnO_4$. (B) forms a derivative (C) with $SOCl_2$, which on reaction with $(CH_3)_2NH$ gives (D). The compound (A) on oxidation with dilute chromic acid gives an unstable compound (E) which decarboxylates readily to give (F), $C_3H_6O$. The compound (F) gives a hydrocarbon (G) on treatment with amalgamated Zn and HCl. Give structures of (A) to (G) with proper reasoning.

**Q.25** A pleasant smelling optically active ester (F) has M.W = 186. It does not react with $Br_2$ in $CCl_4$ Hydrolysis of (F) gives two optically active compounds, (G) soluble in NaOH and (H). (H) gives a positive iodoform test and on warming with cone. $H_2SO_4$ gives (I) (Saytzeff-product) with no geometrical isomers. (H) on treatment with benzene sulfonyl chloride gives (J), which on treatment with NaBr gives optically active (K). When the $Ag^+$ salt of (G) is treated with $Br_2$ racemic (K) is formed. Give structures of (F) to (K) and explain your choices.

**Q.26** Compound (A), M.F $C_6H_{12}O_2$ reduces ammoniacal silver nitrate to metallic silver and loses its optical activity on strong heating yielding (B), $C_6H_{10}O$ which readily reacts with dilute $KMnO_4$. (A) on oxidation with $KMnO_4$ gives (C) having M.F $C_6H_{10}O_3$ which decarboxylates readily on heating to 3–pentanone. The compound (A) can be synthesized from a carbonyl compound having M.F. $C_3H_6O$ on treatment with dilute NaOH. Oxidation of (B) with ammonical silver nitrate followed by acidification gives (D). (D) forms a derivative (E) with SOCl, which on reaction with $H_3CNHCH_2CH_3$ yields (F). Identify (A) to (F) giving proper reaction sequences. What is the name of the reaction involved in the conversion of $C_3H_6O$ to (A)? Give the IUPAC nomenclature of compounds (A) to (F).

**Q.27** A solid organic compound (A), $C_9H_6O_2$ is insoluble in dilute $NaHCO_3$. It produces a dibromoderivative (B), $C_9H_6O_2Br_2$ on treatment with $Br_2/CS_2$. Prolonged boiling of (A) with concentrated KOH solution followed by acidification gives a compound (C), $C_9H_8O_3$. The compound (C) gives effervescence with aqueous $NaHCO_3$ Treatment of (C) with equimolar amount of $Me_2SO_4$/NaOH gives (D), $C_{10}H_{10}O_3$. The compound (D) is identical with the compound prepared from o-methoxy benzaldehyde by condensation with acetic anhydride in the presence of sodium acetate. Treatment of(C) with alkaline $C_6H_5SO_2Cl$ produces (E) which on vigorous oxidation with $KMnO_4$ gives (F). Hydrolysis of(F) gives a steam volatile compound (G) having M.F. $C_7H_6O_3$. Give the structures of(A) to (G) giving the proper reaction sequences.

**Q.28** A neutral compound (A) $C_9H_{16}O_2$on refluxing with dilute alkali followed by acidification yields (B) $C_5H_8O_2$ and (C) $C_4H_{10}O$. (B) liberates $CO_2$ from bicarbonate solution. (C) on dehydration yields 2–butene as the major product. B on treatment with $OsO_4$ followed by reactive hydrolysis gives (D) $C_5H_{10}O_4$ (D) when treated with lead tetraacetate furrnishes acetone and (E) $C_2H_2O_3$. (E) is acidic and reduces Tollen's reagent. Identify (A), (B), (C), (D) and (E) and write the reactions involved.

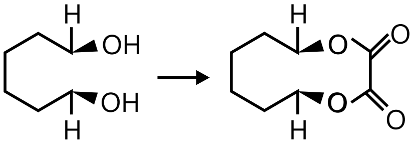
**Q.29** An organic compound A on treatment with ethyl alcohol gives a carboxylic acid B and compound C. Hydrolysis of C under acidic conditions gives B and D. Oxidation of D with $KMnO_4$ also gives B. The compound B on heating with $Ca(OH)_2$ gives E (molecular formula $C_3H_6O$). E does not give Tollen's test and does not reduce Fehling's solution but forms a 2,4–dinitrophenyihydrazone. Identify A, B, C, D and E.

**Q.30** An aqueous alcoholic solution of acetoacetic ester imparts a blue colour with a solution of $FeCl_3$. To this solution if bromine solution is added carefully, the initial colour disappears and the brown colour of bromine appears, which fades soon and the solution after remaining colourless for some time regains the blue violet colour. Explain.

# Exercise 2

## Single Correct Choice Type

**Q.1** Find the reagent used to bring about following conversions.



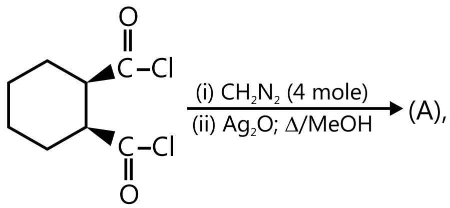
(A) $ClCOCH_2–CH_2$ COCl

(B) $CH_3COOCOCH_3$

(C) $CH_3$ COCl

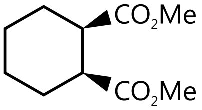
(D) ClCOCOCl

**Q.2**

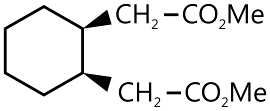


Product (A) of reaction is ?

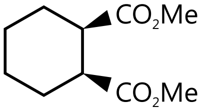
(A)



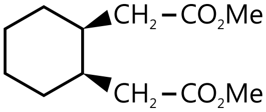
(B)



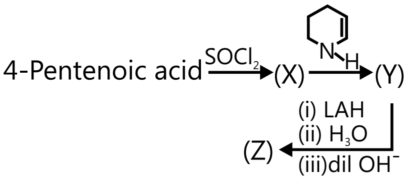
(C)



(D)

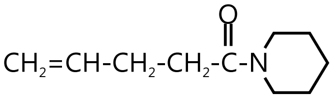


**Q.3**

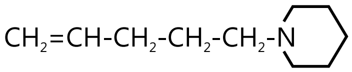


Identify final (major) product :

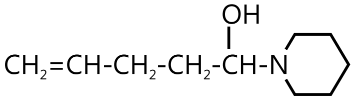
(A)



(B)

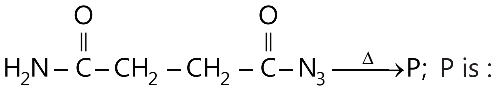


(C)



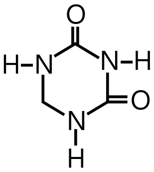
(D) $CH_3–CH_2–CH_2–CH_2–CH_2–OH$

**Q.4**

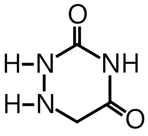


$H_2N-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-N_3 \xrightarrow{\Delta} P$; P is :

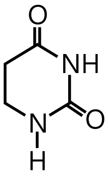
(A)



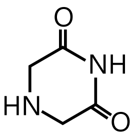
(B)



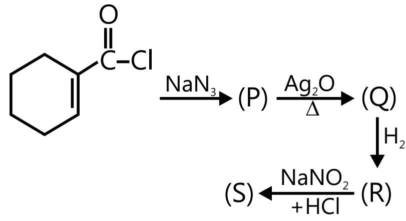
(C)



(D)

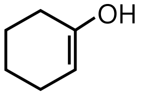


**Q.5**

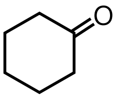


Identify (S) major product:

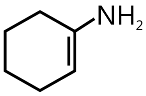
(A)



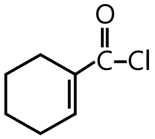
(B)



(C)



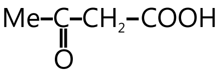
(D)



### Multiple Correct Choice Type

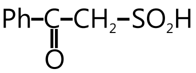
**Q.6** Which will elimination CO$_2$ only on heating

(A)



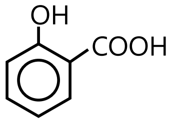
$Me-\underset{\underset{O}{\|}}{C}-CH_2-COOH$

(B)



$Ph-\underset{\underset{O}{\|}}{C}-CH_2-SO_2H$

(C)



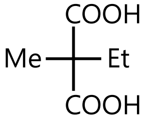
(D) $CH_2=CH–CH_2–COOH$

**Q.7** Methanoic acid and Ethanoic acid can be differentiated by :

(A) Fehling test (B) Iodoform test

(C) Schiff's test (D) NaHCO$_3$ test

### Assertion Reasoning Type



**Q.8 Statement-I:** is optically inactive, it is taken in a glass container and plane polarized light (PPL) is passed through it after heating it for several minutes. The PPL shows significant optical rotation.

**Statement-II:** Like β-keto acid, gem dicarboxylic acid eliminates CO$_2$ on heating.

(A) Statement-I is true, Statement-II is true and Statement-II is correct explanation for Statement-I.

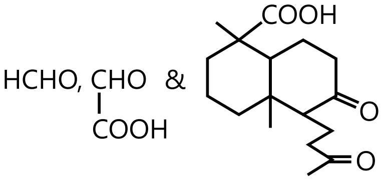
(B) Statement-I is true, Statement-II is true and Statement-II is NOT the correct explanation for Statement-I.

(C) Statement-I is true, Statement-II is false.

(D) Statement-I is false, Statement-II is true.

### Comprehension Type

**Paragraph 1:** Ozonolysis of a compound Agathene dicarboxylic acid gives following compounds:

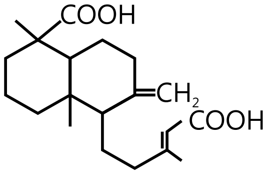


$HCHO,\ \underset{COOH}{\underset{|}{CHO}}\ \&$

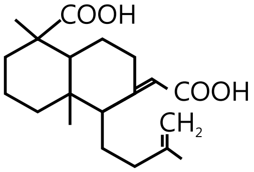
On complete reaction by Na-EtOH Agathene dicarboxylic acid give hydrocarbon $C_{20}H_{38}$ which have 5 chiral carbon in it.

**Q.9** The structure of Agathene dicarboxylic acid is:

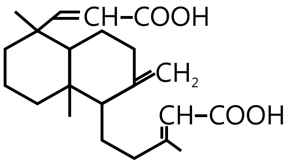
(A)



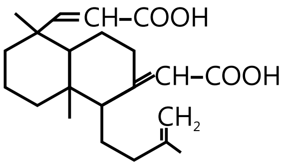
(B)



(C)



(D)



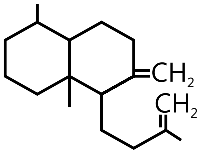
**Q.10** How many chiral carbon are present in Agathene dicarboxylic acid:

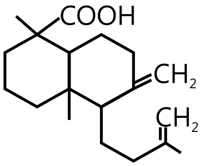
(A) 2 (B) 3 (C) 4 (D) 5

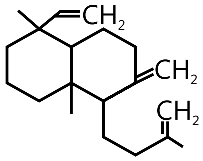
**Q.11** Total stereoisomers possible for Agathene dicarboxylic acid are :

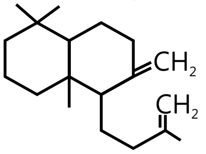
(A) 16 (B) 18 (C) 32 (D) 64

**Q.12** Structure of product formed when Agathene dicarboxylic acid is heated with soda lime is :

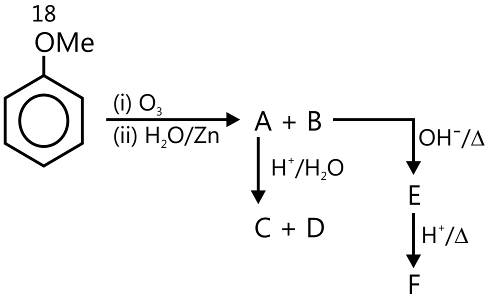
(A) 

(B) 

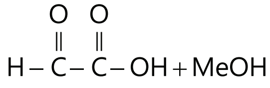
(C) 

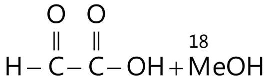
(D) 

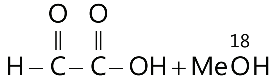
**Paragraph 2:**

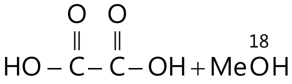


**Q.13** Product C and D are :

(A) 
$\mathrm{H-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH+MeOH}$

(B) 
$\mathrm{H-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH+\overset{18}{M}eOH}$

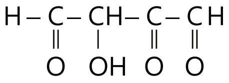
(C) 
$\mathrm{H-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH+Me\overset{18}{O}H}$

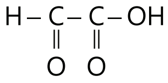
(D) 
$\mathrm{HO-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH+Me\overset{18}{O}H}$

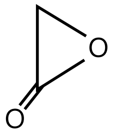
**Q.14** Mechanism for hydrolysis of A will be:

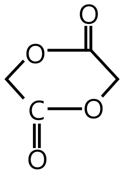
(A) $A_{AC^2}$ (B) $A_{AL^1}$ (C) $A_{AC^1}$ (D) $A_{AL^2}$

**Q.15** F is

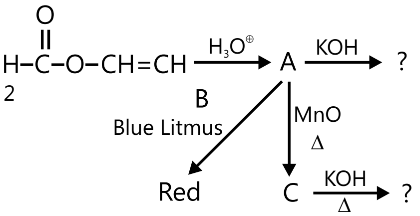
(A) 
$\mathrm{H-\underset{\underset{O}{\|}}{C}-\underset{\underset{OH}{|}}{CH}-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}H}$

(B) 
$\mathrm{H-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-OH}$

(C) 

(D) 

**Paragraph 3:**



**Q.16** Mechanism of formation of A and B is

(A) $A_{AC^2}$ (B) $A_{AC^1}$

(C) $A_{AL^1}$ (D) $A_{AL^2}$

**Q.17** Select true statement:

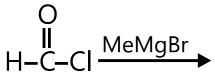
(A) Both B and C give same name reaction with KOH

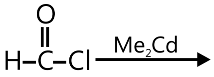
(B) Both B and C give iodoform test

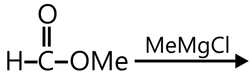
(C) Both B and C give chiral product with PhMgCl followed by $NH_4Cl$

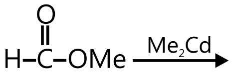
(D) Both B and C are redox reaction

**Q.18** Best method out of the given to prepare B is

(A) 
$\mathrm{H-\overset{\overset{O}{\|}}{C}-Cl}\xrightarrow{\mathrm{MeMgBr}}$

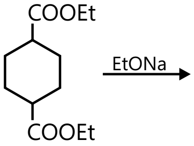
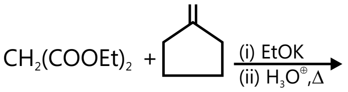
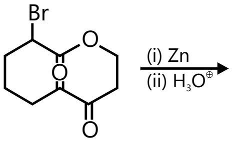
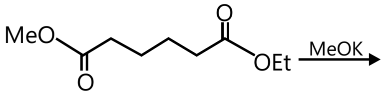
(B) 
$\mathrm{H-\overset{\overset{O}{\|}}{C}-Cl}\xrightarrow{\mathrm{Me_2Cd}}$

(C) 
$\mathrm{H-\overset{\overset{O}{\|}}{C}-OMe}\xrightarrow{\mathrm{MeMgCl}}$

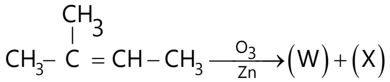
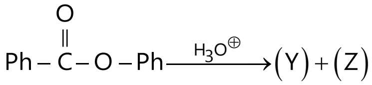
(D) 
$\mathrm{H-\overset{\overset{O}{\|}}{C}-OMe}\xrightarrow{\mathrm{Me_2Cd}}$

## Match the Columns

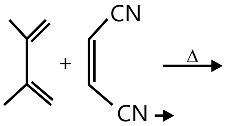
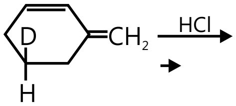
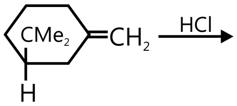
**Q.22** Match reactions given in column I with Names in column II.

| Column I | | Column II | |
|---|---|---|---|
| (A) |  | (p) | Knoevenagel reaction |
| (B) |  | (q) | Perkin reaction |
| (C) |  | (r) | Reformatsky reaction |
| (D) |  | (s) | Dieckmann's condensation |

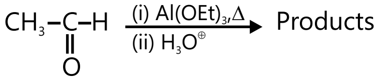
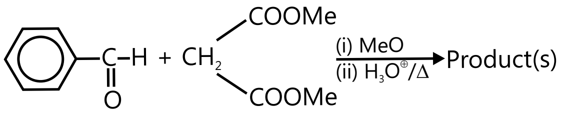
**Q.23**

| Column I | | Column II (Product Differentiate By) | |
|---|---|---|---|
| (A) | $CH_3-CH=CH_2 \xrightarrow[Zn]{O_3} (U)+(V)$ | (p) | By Haloform test |
| (B) |  $CH_3-\overset{CH_3}{\overset{\vert}{C}}=CH-CH_3 \xrightarrow[Zn]{O_3} (W)+(X)$ | (q) | By Fehling test |
| (C) |  $Ph-\overset{O}{\overset{\Vert}{C}}-O-Ph \xrightarrow{H_3O^{\oplus}} (Y)+(Z)$ | (r) | By aq. $NaHCO_3$ |
| | | (s) | By Tollen Test |

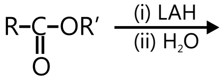
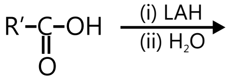
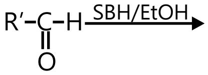
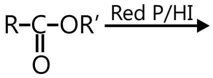
**Q.24**

| Column I (Reactions) | | Column II (Types of Reaction) | |
|---|---|---|---|
| (A) | $CH_3-CH=CH_2 + HCl \rightarrow$ | (p) | Regioselective |
| (B) |  | (q) | Stereoselective |
| (C) |  | (r) | Stereospecific |
| (D) |  | (s) | Diastereomers |
| | | (t) | Cyclic addition |

**Q.25**

| | Column I | | Column II |
|---|---|---|---|
| (A) |  $CH_3-\underset{\underset{O}{\parallel}}{C}-H \xrightarrow[\text{(ii) } H_3O^{\oplus}]{\text{(i) } Al(OEt)_3, \Delta} \text{Products}$ | (p) | One of the organic product formed will decolourise bromine water |
| (B) |  | (q) | One of the organic product formed will give brisk effervescence with $NaHCO_3$ |
| (C) | $\text{PhMgCl} \xrightarrow[\text{(ii) } H^{\oplus} \text{ (iii) } SOCl_2 \text{ (iv) MeMgCl}]{\text{(i) } CO_2} \text{Products}$ | (r) | One of the organic product formed will give haloform test. |
| | | (s) | One of the organic product formed will give 2, 4 DNP test |

**Q.26**

| | Column I (Reaction) | | Column II (Product obtained by reaction) |
|---|---|---|---|
| (A) |  $R-\underset{\underset{O}{\parallel}}{C}-OR' \xrightarrow[\text{(ii) } H_2O]{\text{(i) LAH}}$ | (p) | $R'-CH_3$ |
| (B) |  $R'-\underset{\underset{O}{\parallel}}{C}-OH \xrightarrow[\text{(ii) } H_2O]{\text{(i) LAH}}$ | (q) | $R'-OH$ |
| (C) | $R'-CH_2-Br \xrightarrow{LAH}$ | (r) | $R'-CH_2-OH$ |
| (D) |  $R'-\underset{\underset{O}{\parallel}}{C}-H \xrightarrow{SBH/EtOH}$ | (s) | $R'-H$ |
| (E) |  $R-\underset{\underset{O}{\parallel}}{C}-OR' \xrightarrow{\text{Red P/HI}}$ | (t) | $R-CH_3$ |

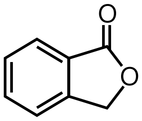
## Previous Years' Questions

**Q.1** When benzene sulphonic acid and p–nitrophenol are treated with $NaHCO_3$, the gases released respectively, are ***(2006)***

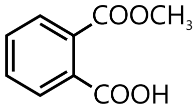
(A) $SO_2$, $NO_2$ (B) $SO_2$, NO

(C) $SO_2$, $CO_2$ (D) $CO_2$, $CO_2$

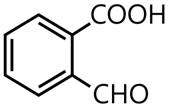
**Q.2** Which of the following reactants on reaction with conc. NaOH followed by acidification gives the following lactone as the only product? ***(2006)***



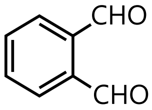
(A)



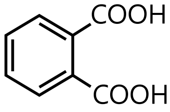
(B)



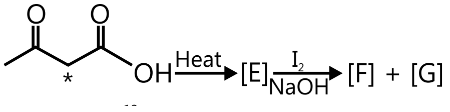
(C)



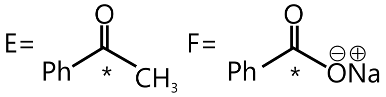
(D)



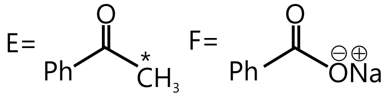
**Q.3** In the following reaction sequence, the correct structures of E, F and G are



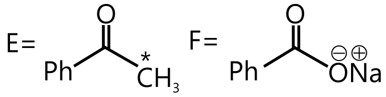
(* implies $^{13}C$ labelled carbon) ***(2008)***

(A)


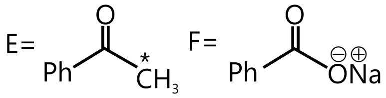
$G=CHI_3$

(B)


$G=CHI_3$

(C)


$G=\overset{*}{C}HI_3$

(D)


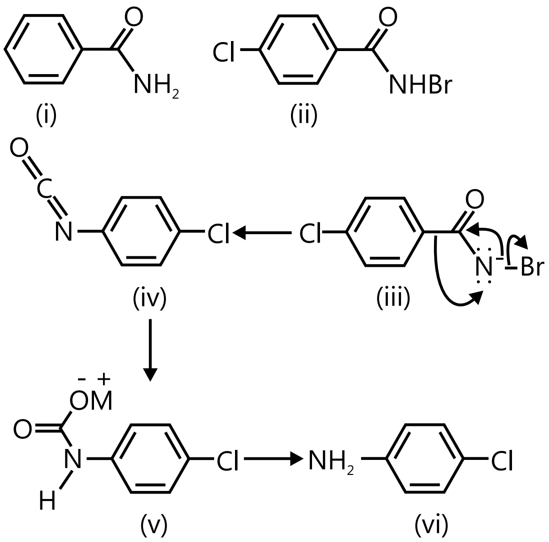
$G=\overset{*}{C}H_3I$

**Q.4** Reaction of $RCONH_2$ with a mixture of $Br_2$ and KOH gives $R–NH_2$ as the main product. The intermediates involved in this reaction are : ***(1992)***

(A) RCONHBr (B) RNHBr

(C) R–N=C=O (D) $RCONBr_2$

**Comprehension:** $RCONH_2$ is converted into $RNH_2$ by means of Hofmann bromamide degradation.



In this reaction, RCONHBr is formed from which this reaction has derived its name. Electron donating group at phenyl activates the reaction. Hofmann degradation reaction is an intramolecular reaction. ***(2006)***

**Q.5** How can the conversion of (i) to (ii) be brought about ?

(A) KBr (B) KBr + $CH_3ONa$

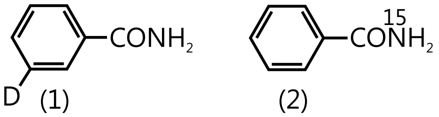
(C) KBr + KOH (D) $Br_2$ + KOH

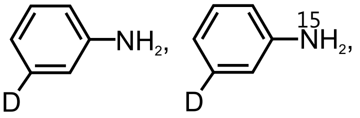
**Q.6** Which is the determining step in Hofmann bromamide degradation ?

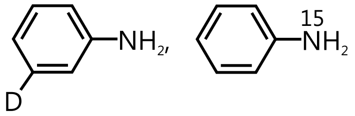
(A) Formation of (i) (B) Formation of (ii)

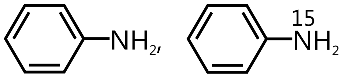
(C) Formation of (iii) (D) Formation of (iv)

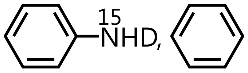
**Q.7** What are the constituent amine formed when the mixture of (1) and (2) undergoes Hofmann bromamide degradation ?



(A)


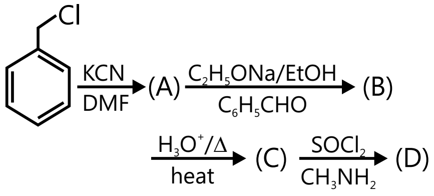
(B)


(C)


(D)


**Q.8** (±) 2-Phenylpropanoic acid on treatement with (+) 2-butanol gives (A) and (B). Deduce their structures and also establish stereochemical relation between them. ***(2003)***

**Q.9** Compound A of molecular formula $C_9H_7O_2Cl$ exists in keto from and predominantly in enolic form B. On oxidation with $KMnO_4$, A gives m-chlorobenzoic acid. Identify A and B. ***(2003)***

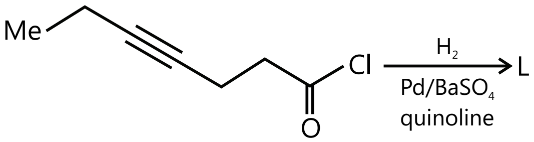
**Q.10**


Identify A to D. ***(2004)***

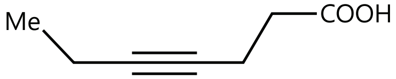
### Paragraph 1 (Questions 11 to 12)

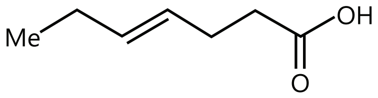
In the following sequence, products I, J and L are formed. K represents a reagent.

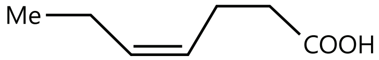
$$\text{Hex-3-ynal} \xrightarrow[\text{2. PBr}_3]{\text{1. NaBH}_4} \text{I} \xrightarrow[\text{3. H}_3\text{O}^+]{\text{1. Mg/ether} \quad \text{2.CO}_2} \text{J} \xrightarrow{\text{K}}$$

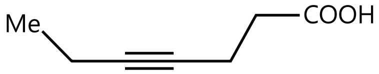


**Q.11** The structures of compounds J and K respectively are **(2008)**

(A)  and $SOCl_2$

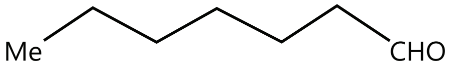
(B)  and $SOCl_2$

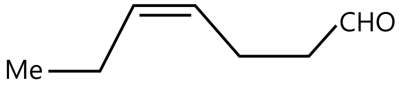
(C)  and $SOCl_2$

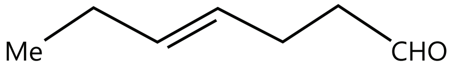
(D)  and $CH_3SO_2Cl$

**Q.12** The structure of product L is: **(2008)**

(A) 

(B) 

(C) 

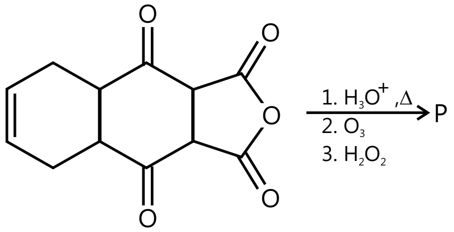
(D) 

**Q.13** The carboxyl functional group (–COOH) is present in **(2012)**

(A) Picric acid (B) Barbituric acid

(C) Ascorbic acid (D) Aspirin

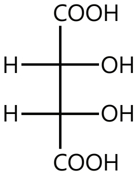
**Q.14** The total number of carboxylic acid groups in the product P is: **(2013)**



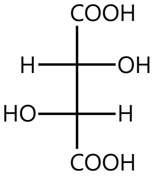
### Paragraph 2 (Questions 15 to 16)

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

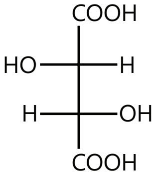
Upon treatment with dilute alkaline $KMnO_4$, P as well as Q could produce one or more than one from S, T and U.



S



T



U

**Q.15** Compounds formed from P and Q are, respectively **(2013)**

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

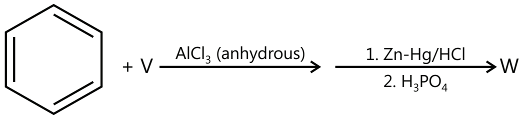
(B) Optically inactive S and optically inactive pair (T, U)

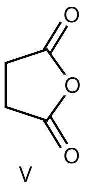
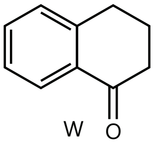
(C) Optically active pair (T, U) and optically active S

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

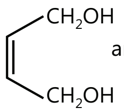
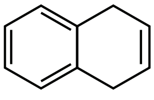
**Q.16** In the following reaction sequences V and W are, respectively **(2013)**

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

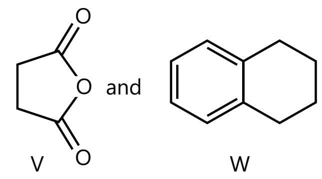


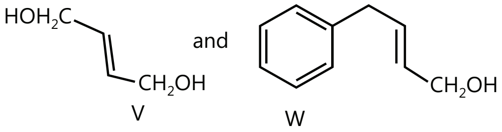
(A)  and 

V W

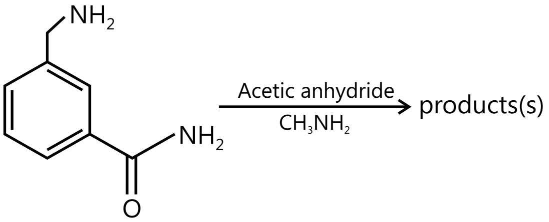
(B)  and 

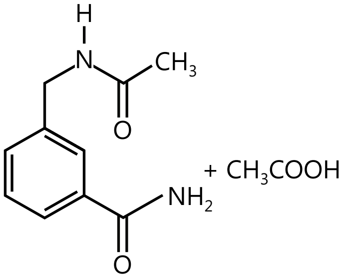
V W

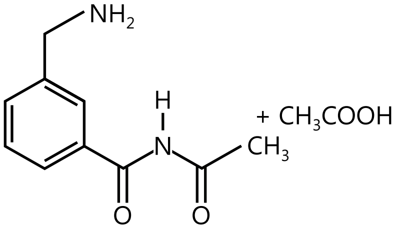
(C) 

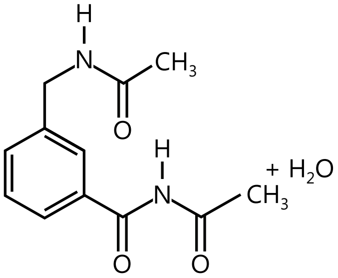
(D) 

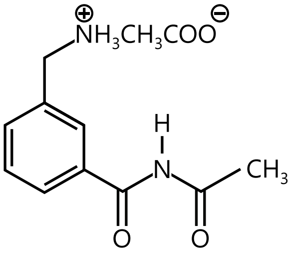
**Q.17** In the reaction shown below, the major product(s) formed is/are ***(2014)***



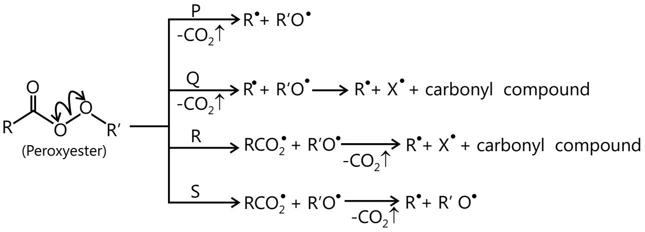
(A) 

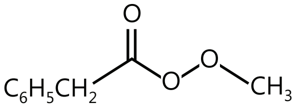
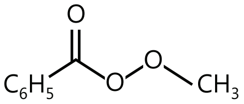
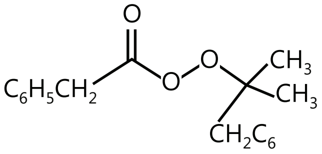
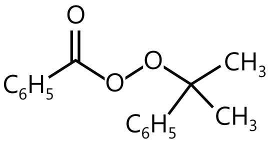
(B) 

(C) 

(D) 

**Q.18** Different possible thermal decomposition pathways for peroxyesters are shown below. Match each pathway from list I with an appropriate structure from list II and select the correct answer using the code given below the lists. ***(2014)***

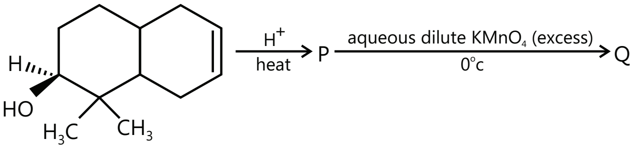


| | **List I** | | **List II** |
|---|---|---|---|
| (i) | Pathway P | (p) |  |
| (ii) | Pathway Q | (q) |  |
| (iii) | Pathway R | (r) |  |
| (iv) | Pathway S | (s) |  |

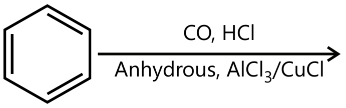
Code:

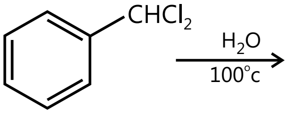
| | (i) | (ii) | (iii) | (iv) |
|---|---|---|---|---|
| (A) | p | r | s | q |
| (B) | q | s | r | p |
| (C) | s | p | q | r |
| (D) | r | q | p | s |

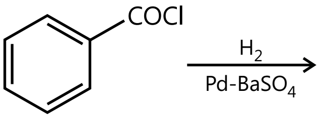
**Q.19** The number of hydroxyl group(s) in Q is ***(2015)***

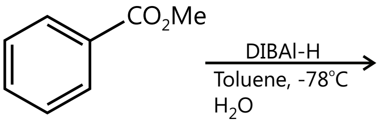


**Q.20** Among the following, the number of reaction(s) that produce(s) benzaldehyde is **_(2015)_**

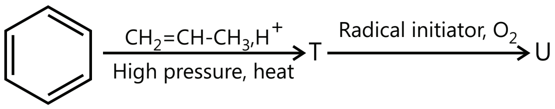
(A)


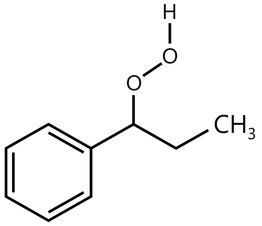
(B)


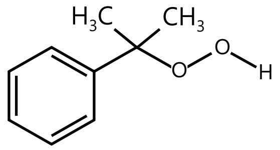
(C)


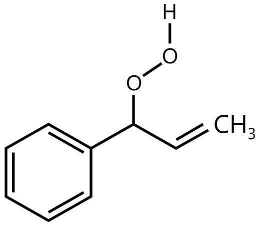
(D)


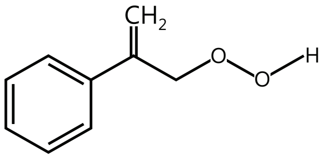
**Q.21** The major product U in the following reactions is **_(2015)_**



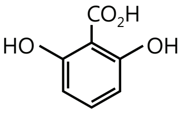
(A)


(B)


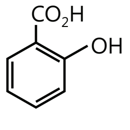
(C)


(D)


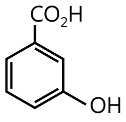
**Q.22** The correct order of acidity for the following compounds is **_(2013)_**



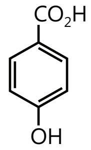
(I)



(II)



(III)

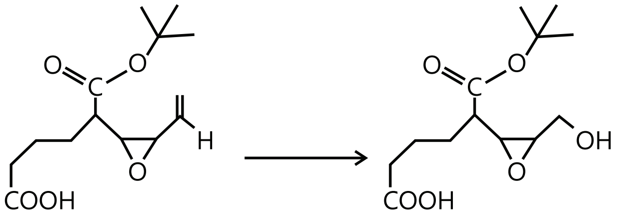


(IV)

(A) I > II > III > IV (B) III > I > II > IV

(C) III > IV > II > I (D) I > III > IV > II

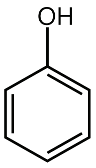
**Q.23** Reagent(s) which can be used to bring about the following transformation is(are) **(2016)**



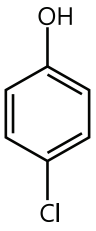
(A) $LiAlH_4$ in $(C_2H_5)_2O$ (B) $BH_3$ in THF

(C) $NaBH_4$ in $C_2H_5OH$ (D) Raney $Ni/H_2$ in THF

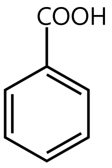
**Q.24** The correct acidity order of the following is **_(2009)_**



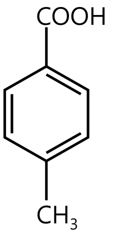
(I)



(II)



(III)

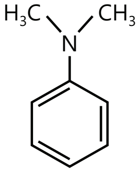


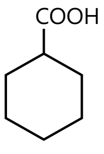
(IV)

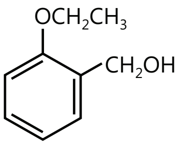
(A) (III) > (IV) > (II) > (I) (B) (IV) > (III) > (I) > (II)

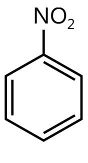
(C) (III) > (II) > (I) > (IV) (D) (II) > (III) > (IV) > (I)

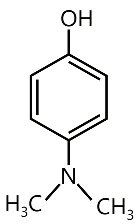
**Q.25** Amongst the following, the total number of compounds soluble in aqueous NaOH is : **_(2010)_**

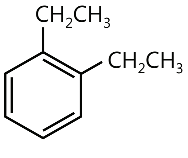


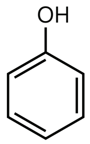


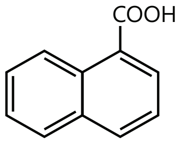




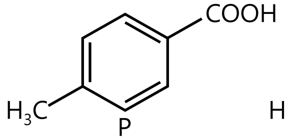




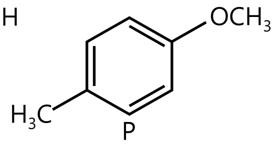




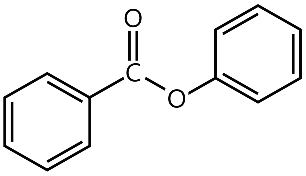
**Q.26** The compounds P, Q and S *(2010)*



P



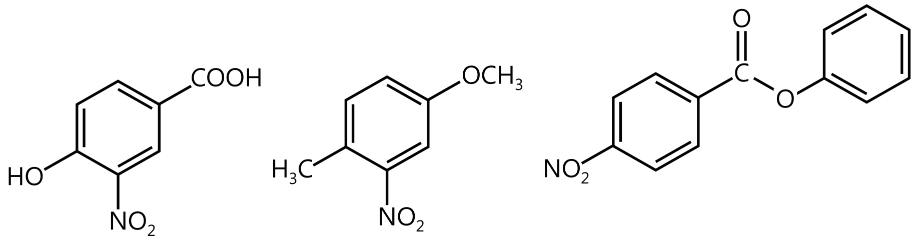
P



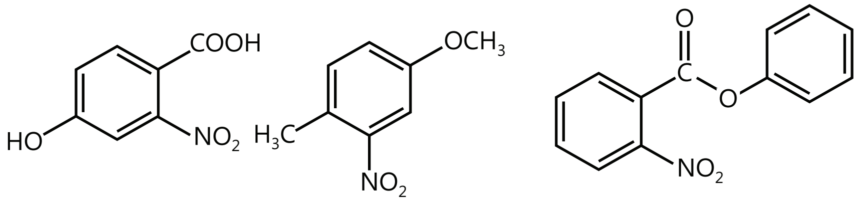
S

were separately subjected to nitration using $HNO_3/H_2SO_4$ mixture. The major product formed in each case respectively, is

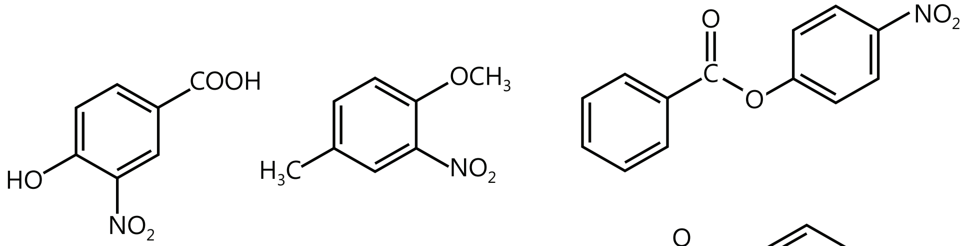
(A)



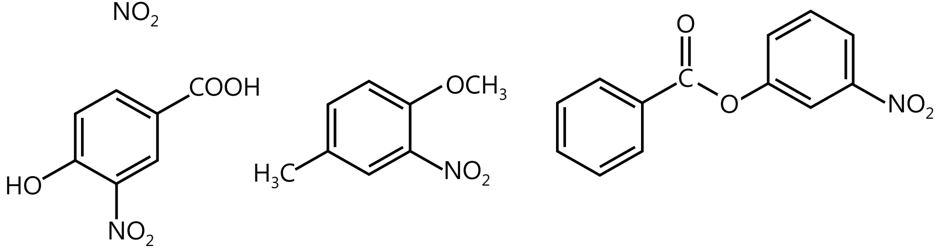
(B)



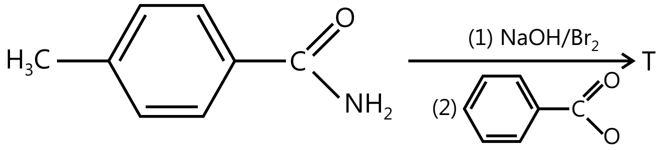
(C)

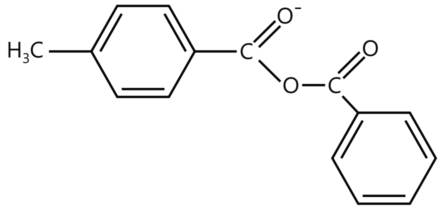


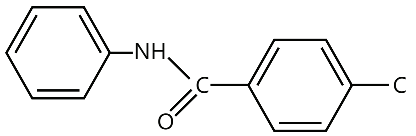
(D)

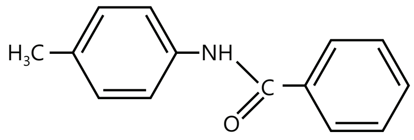


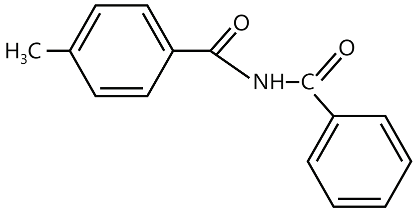
**Q.27** *(2010)*



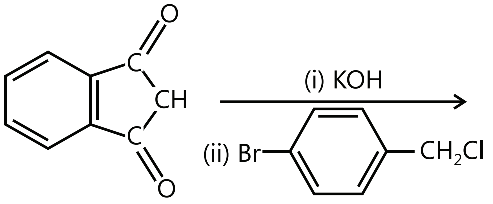
(A)


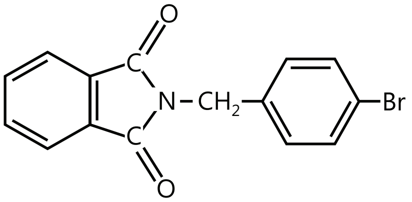
(B)


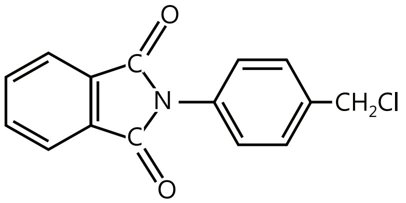
(C)


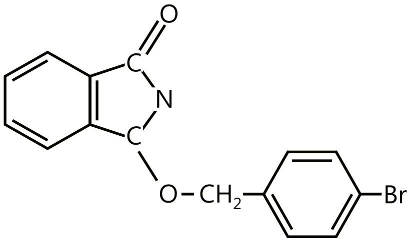
(D)


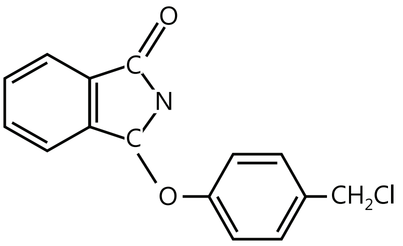
**Q.28** The major product of the following reaction is ***(2011)***



(A)


(B)


(C)


(D)


**Q.29** Among the following compounds, the most acidic is ***(2011)***

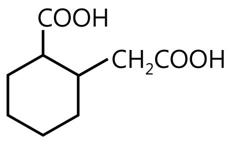
(A) p-nitrophenol

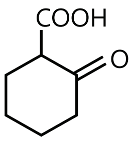
(B) p-hydroxybenzoic acid

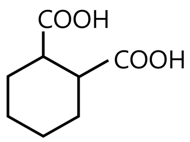
(C) o-hydroxybenzoic acid

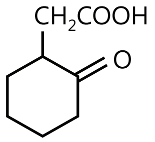
(D) p-toluic acid

**Q.30** The compound that undergoes decarboxylation most readily under mild condition is ***(2011)***

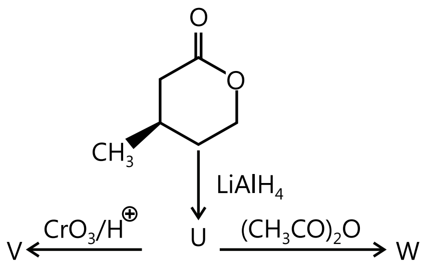
(A)


(B)


(C)


(D)


**Q.31** With reference to the scheme given, which of the given statements about T,U,V and W is correct? ***(2012)***



(A) T is soluble in hot aq. NaOH

(B) U is optically active

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

(D) V gives effervescence on treatment with aq. $NaHCO_3$

# MASTERJEE Essential Questions

## JEE Main/Boards

### Exercise 1

Q.2 Q.8 Q.17
Q.21 Q.25 Q.29

### Exercise 2

Q.1 Q.4 Q.7
Q.13

### Previous Years' Questions

Q.1 Q.10 Q.12
Q.17 Q.21

## JEE Advanced/Boards

### Exercise 1

Q.2 Q.8 Q.18
Q.22 Q.25 Q.30

### Exercise 2

Q.4 Q.6 Q.9
Q.14 Q.18

### Previous Years' Questions

Q.2 Q.8 Q.14
Q.21 Q.25 Q.31

# Answer Key

## JEE Main/Boards

### Exercise 2

**Q.1** B **Q.2** A **Q.3** D **Q.4** C **Q.5** B **Q.6** A
**Q.7** B **Q.8** B **Q.9** D **Q.10** D **Q.11** B **Q.12** A
**Q.13** B **Q.14** C **Q.15** C **Q.16** C **Q.17** B **Q.18** B
**Q.19** D

### Previous Years' Questions

**Q.1** D **Q.2** C **Q.3** C **Q.4** A **Q.5** D **Q.6** B
**Q.7** C **Q.8** D **Q.9** False **Q.10** False **Q.11** D **Q.12** C
**Q.13** B **Q.14** C **Q.15** C **Q.15** C **Q.16** D **Q.17** D
**Q.18** A **Q.19** C **Q.20** D **Q.21** C

# JEE Advanced/Boards

## Exercise 2

### Single Correct Choice Type

**Q.1** D **Q.2** B **Q.3** B **Q.4** C **Q.5** B

### Multiple Correct Choice Type

**Q.6** A, C, D **Q.7** A, C

### Assertion Reasoning Type

**Q.8** D

### Comprehension Type

**Q.9** A **Q.10** C **Q.11** C **Q.12**A **Q.13** C **Q.14** A

**Q.15** D **Q.16** A **Q.17** D **Q.18** B

### Match the Columns

**Q.19** A → s; B → p; C → r; D → s

**Q.20** A → p; B → q, s; C → r

**Q.21** A → p; B → r, t; C → p, s; D → p, q, s

**Q.22** A → q, r; B → p, q; C → r, s

**Q.23** A → q, ; B → r; C → p; D → r; E → s, t

## Previous Years' Questions

**Q.1** D **Q.2** C **Q.3** C **Q.4** A, C **Q.5** D **Q.6** D

**Q.7** B **Q.11** A **Q.12** C **Q.13** D **Q.14** B **Q.15** B

**Q.16** A **Q.17** A **Q.18** A **Q.19** D **Q.20** A, B, C, D **Q.21** B

**Q.22** A **Q.23** C **Q.24** A **Q.25** 5 **Q.26** C **Q.27** C

**Q.28** A **Q.29** C **Q.30** B **Q.31** A, C, D

# Solutions

## JEE Main/Boards

## Exercise 1

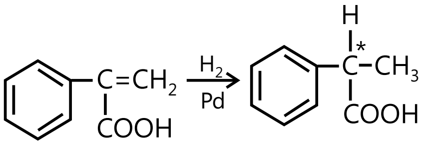
**Sol 1:** The uptake of 2H atoms shows the presence of one >C=C< along with $C_6H_5$– and –COOH, which accounts for the 6° unsaturation.. Furthermore H and I are monosubstituted benzene derivatives.

H is $C_6H_5$–C(COOH)=$CH_2$ giving

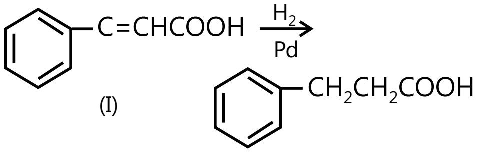
$H_3CCHC_6H_5COOH$ with one asymmetric carbon atom.

I is $C_6H_5CH$=CHCOOH, giving

$C_6H_5CH_2CH_2COOH$ with no asymmetric carbon.



(H)



(I)

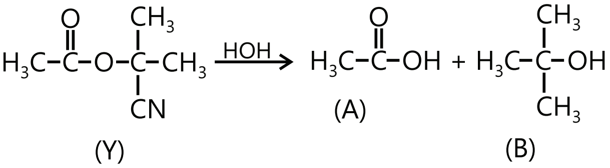
**Sol 2:** (A) = $C_{15}H_{31}CH_2OH$,

(B) = $C_{15}H_{31}CH_2Cl$,

(C) = $C_{15}H_{31}CH_2CH_2CH_2OH$,

(D) = $C_{15}H_{31}CH_2CH_2COOH$.

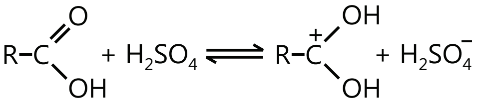
**Sol 3:** (Y) is an ester because it is hydrolysed to acid and alcohol. Since the alcohol is not oxidized by acidified $KMnO_4$ and gives cloudiness at once with Lucas reagent, hence it is a t-alcohol.

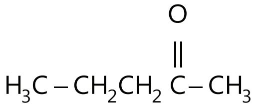


**Sol 4:** This is because $C_2H_5OH$ undergoes dehydration to form $C_2H_4$ at 170°C in presence of excess of conc. $H_2SO_4$.

$$CH_3-CH_2OH \xrightarrow[170^\circ C]{H_2SO_4(conc.)} H_2O+CH_2=CH_2$$

**Sol 5:** In the presence of strong acids, the $H^{\oplus}$ is captured by the carboxylic acid and the following equilibrium is established:

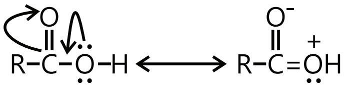


**Sol 6:** 

$$H_3C-CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

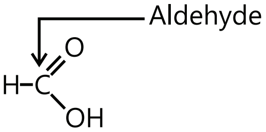
**Sol 7:** It is because the carboxylate group (–COO⁻) of the branched acid is more shielded from the solvent molecules, there, it cannot be stabilized effectively by salvation.

**Sol 8:** It is because carboxylic group does not have true carbonyl group due to resonance.



Due to resonance >C=O bond of –COOH develops partial double bond character and cannot show reactions with hydroxylamine, phenyl hydrazine, etc.

**Sol 9:** It is because formic acid combines the properties of both an aldehyde an acid.



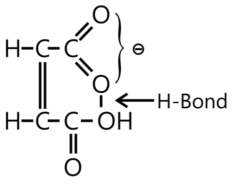
Hence it has reducing character of aldehydes.

$HCOOH + 2(Ag(NH_3)_2)^+OH^- \xrightarrow{\Delta}$

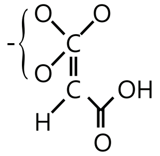
$HCOONH_4 + 3NH_3 + H_2O + 2Ag\downarrow$

or $HCOOH + Ag_2O \rightarrow CO_2 + H_2O + 2Ag\downarrow$

**Sol 10:** Both these unsaturated acids have two ionisable hydrogens. After the release of first hydrogen, second hydrogen of maleiate ions is involved in H-bonding, whereas no H-bonding is possible in fumarate ion.



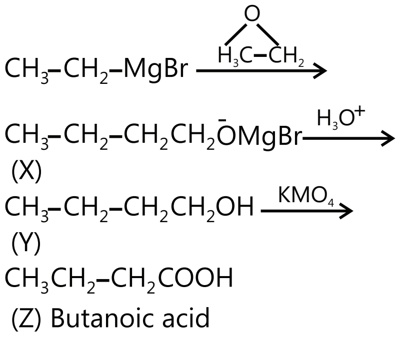
(Maleiate ion)



(Fumarate ion
(H-bond not possible)

Due to the formation of H-bond in maleiate ion more energy is required to remove H$^{\oplus}$ from it than from fumarate ion, in which H$^{\oplus}$ release is easy comparatively. Thus, $K_2$ for fumaric acid is more than maleic acid.

**Sol 11:**



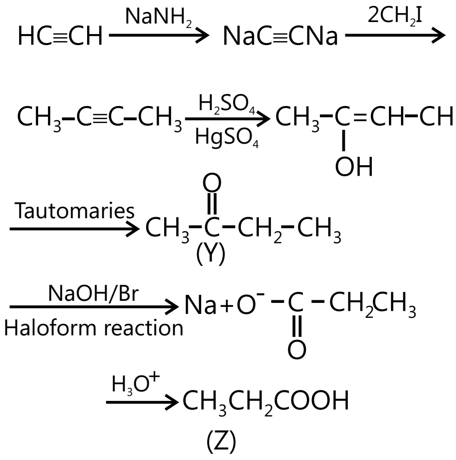
$CH_3-CH_2-MgBr \xrightarrow{\overset{O}{H_3C-CH_2}}$

$CH_3-CH_2-CH_2CH_2\bar{O}MgBr \xrightarrow{H_3O^+}$
(X)

$CH_3-CH_2-CH_2CH_2OH \xrightarrow{KMO_4}$
(Y)

$CH_3CH_2-CH_2COOH$
(Z) Butanoic acid

**Sol 12:**



$HC\equiv CH \xrightarrow{NaNH_2} NaC\equiv CNa \xrightarrow{2CH_2I}$

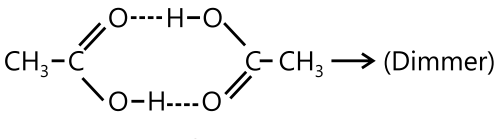
$CH_3-C\equiv C-CH_3 \xrightarrow[HgSO_4]{H_2SO_4} CH_3-\underset{OH}{C}=CH-CH_3$

$\xrightarrow{Tautomaries} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$
(Y)

$\xrightarrow[\text{Haloform reaction}]{NaOH/Br} Na+O^- - \underset{O}{\underset{\|}{C}} - CH_2CH_3$

$\xrightarrow{H_3O^+} CH_3CH_2COOH$
(Z)

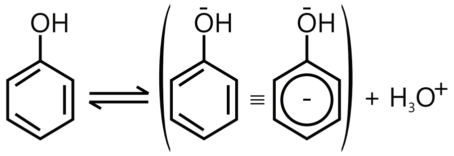
**Sol 13:**

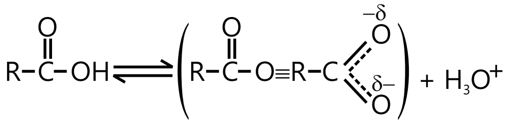


Dimerization of acetic acid occur in benzene via intermolecular H-bonding Hydrogen bond is a special type of dipole-attraction.

**Sol 14:** sp hybridized carbon of –C≡C– of acid (I) and sp$^2$ hybridized carbon of –C=C– of acid (II) attract the bonded electron more than do the sp$^3$ – hybridized carbon atoms. Consequently –C ≡ C– and –C ≡ C– are acid strengthening EWG's (Electron withdrawing group, stabilizes anion, thus strengthens acid) This makes $CH_3CH_2COOH$ weaked of all these three acids since –C ≡ C– is more acid strengthens group than –C ≡ C– group. This makes acid (I) stronger than acid (II)

**Sol 15:**





The electron charge in carboxylate ion is more dispersed in comparison to phenoxide ion, since there are two electro negative oxygen carboxylate ion as compared to oxygen atom in phenoxide ion.

**Sol 16:** $CH_3COCl$ will after least stearic hindrance hence it hydrolysis will be more vigorous.

**Sol 17:** Amide = $CH_3CONH_2$ Therefore acid is $CH_3COOH$

**Sol 18:** Acid (Y) obtained after decarboxylation must be mono carboxylic acid thus molecular weight = Equivalent weight

The acid must Be (COOH → 45g/mol) Given mass = 60g ; ∴ = 60 – 45 = 15g/mol

Which is definitely due to – $CH_3$

Hence Y is $CH_3COOH$

Carboxylic acid (X) has second COOH replacing H of $CH_3COOH$

SO (X) is malonic $CH_2(COOH)_2$ of molecular mass 60 + 44 = 104

Since it has two group so its equivalent mass = 104/2 = 52b/eq.

**Sol 19:** Dehydration occur with all the three reagent

$$C_2H_5CH_2CONH_2 \xrightarrow{P_2O_5} C_6H_5CH_2CN + H_2O$$

$$C_6H_5CH_2CONH_2 \xrightarrow{SOCl_2} C_6H_5CH_2CN + 2HCl + SO_2$$

$$C_6H_5CH_2CONH_2 \xrightarrow[PCl_5]{POCl_3\ Or} C_6H_5CH_2CN + H_2O$$

**Sol 20:** As the size of the substituent on $\alpha$-carbon increases, the tetrahedral bonded intermediate become more crowded. The greater the crowding the slower is the reaction.

**Sol 21:** (A) $(CH_3CO)_2O$ (Acetic anhydride)

(B) $CH_3COOH$ (Ethanoic acid)

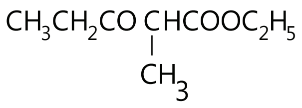
(C) $CH_3COOC_2H_5$ (Ethyl ethanoate)

(D) $C_3H_5OH$ (Ethanol)

(E) $CH_3COCH_3$

**Sol 22:** (A) $CH_3CH_2COOC_2H_5$ (Ethyl propionate)

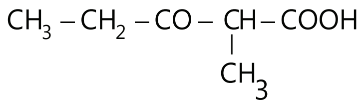
(B)



$$CH_3CH_2CO\underset{\underset{CH_3}{|}}{C}HCOOC_2H_5$$

Ethyl-(3-keto 2-methylpentanoic acid)

(C)



$$CH_3-CH_2-CO-\underset{\underset{CH_3}{|}}{C}H-COOH$$

3-Keto-2-methylpentanoic acid

**Sol 23:** (A) $CH_3CH_2CH_2CH_2COOCH_2CH_3$

or $CH_3COOCH_2CH_2CH_2CH_3$

(B) $C_2H_5OH$

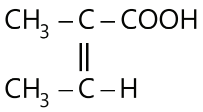
(C) $CH_3CH_2CH_2CH_2OH$

(D) $CH_3CHO$

(E) $CH_3CH=CHCHO$

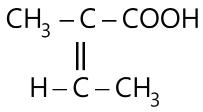
(F) $CH_3COOH$

**Sol 24:** (A)



$$\begin{array}{c} CH_3-C-COOH \\ \| \\ CH_3-C-H \end{array}$$

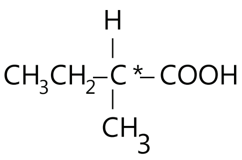
Cis



$$\begin{array}{c} CH_3-C-COOH \\ \| \\ H-C-CH_3 \end{array}$$

Trans

(B)



$$CH_3CH_2-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}{}^{*}-COOH$$

(2-methylbutanoic acid)

**Sol 25:** (A) $HCOOH$
(B) $CO$
(C) $(COOH)_2$

**Sol 26:** A = $CH_3OH$ (Methanol)

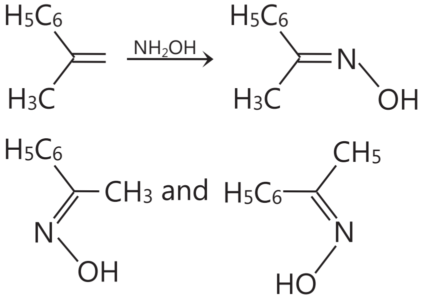
B = $CH_3COCH_3$ (Methyl ethanoate)

C = $HCHO$ (Methanal)

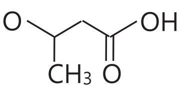
D = $HCOOH$ (Methanoic acid)

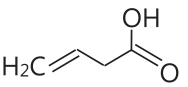
E = $HCONH_2$ (Formamide or methanamide)

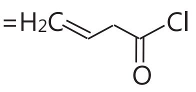
**Sol 27:**

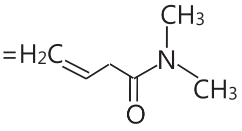


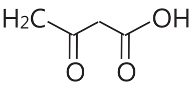
**Sol 28:**

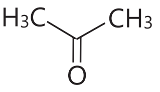
A=


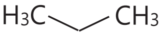
B=


C=


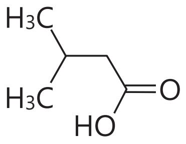
D=


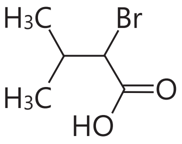
E=


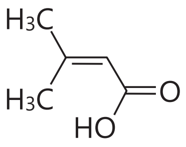
F=


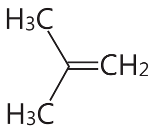
G=


**Sol 29:**

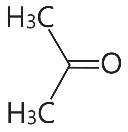
A =


B =


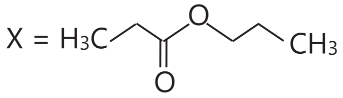
C =


D =


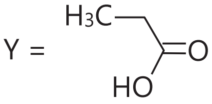
E = HCHO

F =


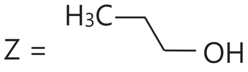
**Sol 30:**



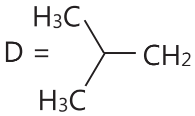
Propyl propionate



Propionic acid



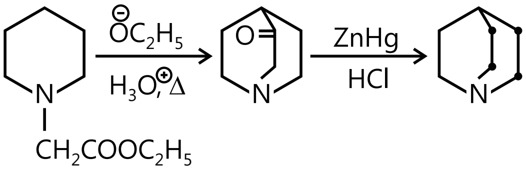
Propan-1-ol



## Exercise 2

### Single Correct Choice Type

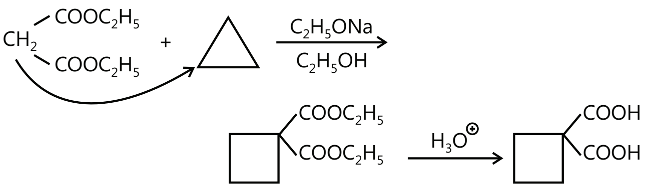
**Sol 1: (B)**



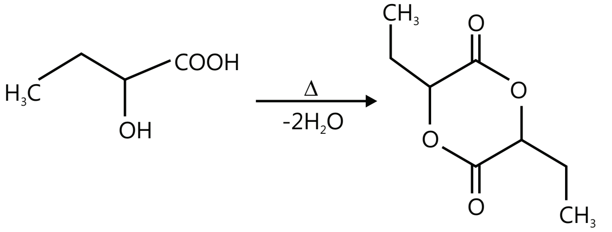
**Sol 2**: **(A)** MeCOCl > $MeCON_3$ > MeCOOCOMe. Consider electronegativity of halogen, azide & ester.

Halogen is on top, since it has the highest electronegativity.

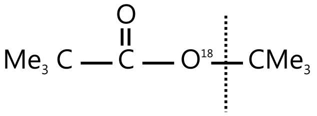
**Sol 3: (D)**



**Sol 4: (C)**



**Sol 5: (B)** Acid catalyzed alkyl cleavage

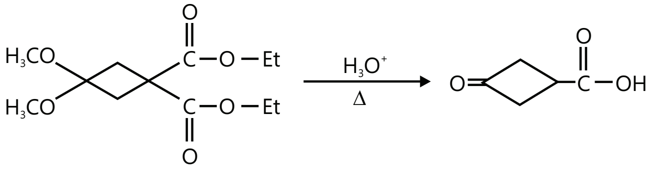


$$Me_3C-\overset{\overset{\displaystyle O}{\|}}{C}-O^{18}-CMe_3$$

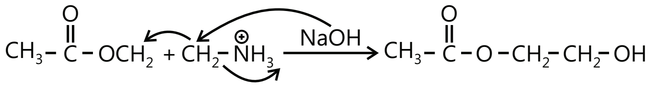
**Sol 6: (A)**

$CH_3CH_2CONH_2 \xrightarrow[\Delta]{PCl_5} CH_3CH_2CN$ -Reduction

**Sol 7: (B)**

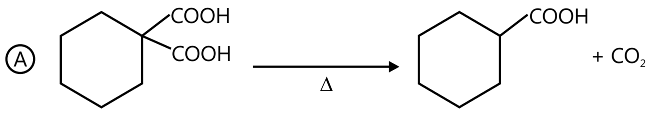


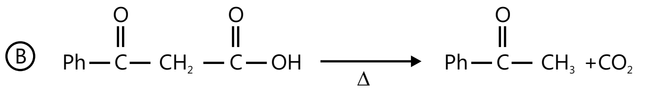
**Sol 8: (B)**

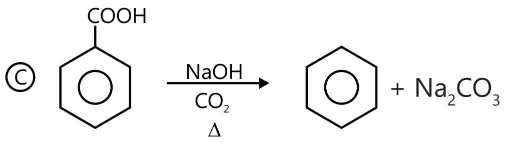


**Sol 9: (D)** Reduction reactions.

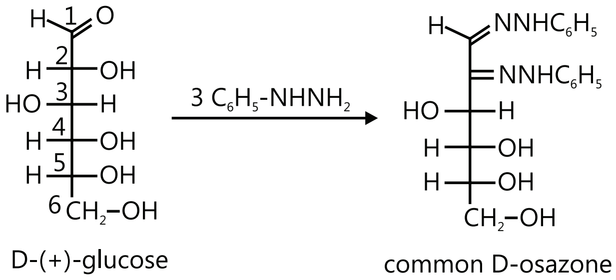
**Sol 10: (D)**

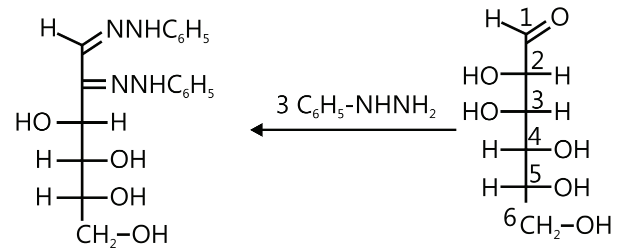






**Sol 11: (B)**

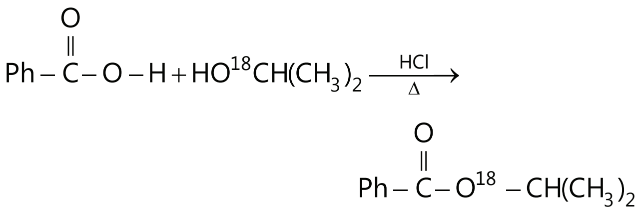




common D-osazone

D-(+)-mannose

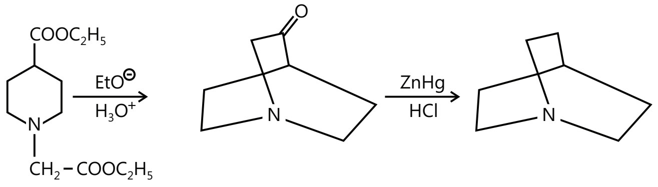
**Sol 12: (A)** Esterification.



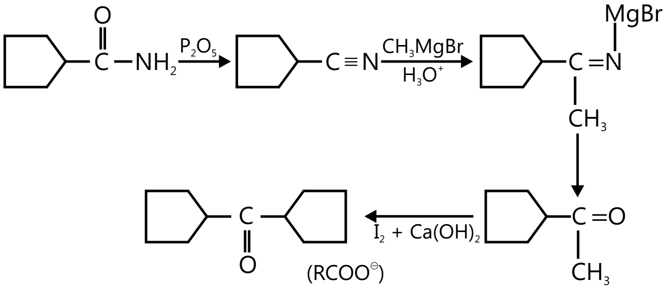
$$Ph-\overset{\overset{O}{\|}}{C}-O-H+HO^{18}CH(CH_3)_2 \xrightarrow[\Delta]{HCl} Ph-\overset{\overset{O}{\|}}{C}-O^{18}-CH(CH_3)_2$$

**Sol 13: (B)** Dieckmann condensation product.

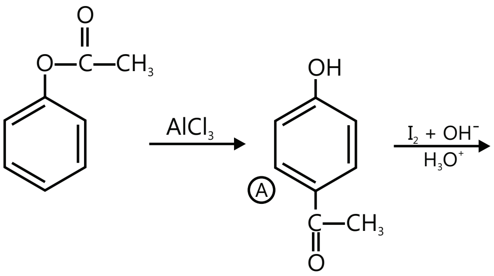
**Sol 14: (C)**

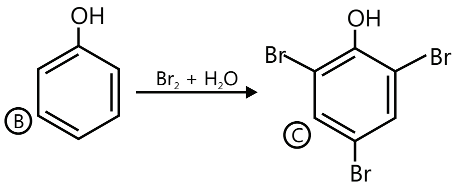


**Sol 15: (C)**



**Sol 16: (C)**





**Sol 17: (B)** Since it lacks active methylene componenet stable anion formation does not take place and thus it can not undergo self condensation reaction.

**Sol 18: (B)** Esterification.

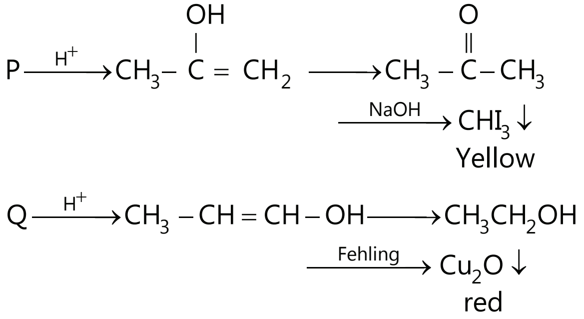
**Sol 19: (D)** Self-explanatory reactions

## Previous Years' Questions

**Sol 1: (D)** $CH_3–CH_2–COOH + NaHCO_3 \rightarrow$
$CH_3CH_2COONa + H_2O + \overset{*}{C}O_2$

**Sol 2: (C)** $C_6H_5COOH + SOCl_2 \rightarrow C_6H_5–COCl$

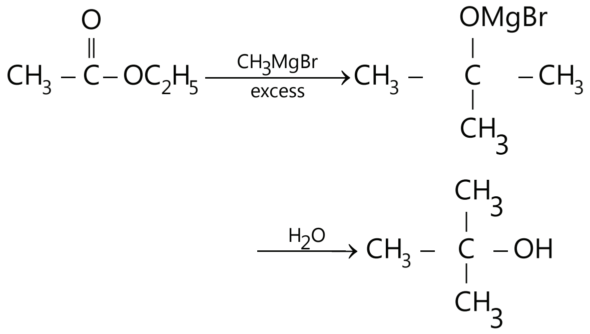
**Sol 3: (C)**



$$P \xrightarrow{H^+} CH_3-\overset{\overset{OH}{|}}{C}=CH_2 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{NaOH} \underset{\text{Yellow}}{CHI_3\downarrow}$$

$$Q \xrightarrow{H^+} CH_3-CH=CH-OH \longrightarrow CH_3CH_2OH \xrightarrow{Fehling} \underset{\text{red}}{Cu_2O\downarrow}$$

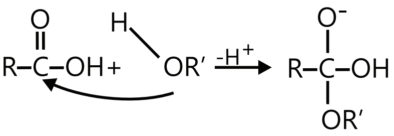
**Sol 4: (A)**



$$CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow[excess]{CH_3MgBr} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OMgBr}{|}}{C}}-CH_3$$

$$\xrightarrow{H_2O} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

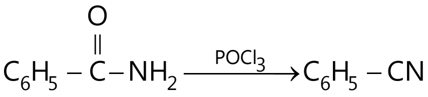
**Sol 5: (D)**



$$R-\overset{O}{\overset{\|}{C}}-OH+H-OR'\xrightarrow{-H^+}R-\underset{OR'}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-OH$$

Reaction occur at planar $sp^2$ carbon giving racemic mixture of product.

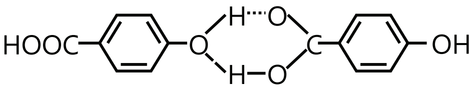
**Sol 6: (B)**



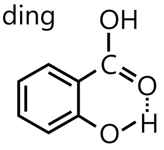
$$C_6H_5-\overset{O}{\overset{\|}{C}}-NH_2\xrightarrow{POCl_3}C_6H_5-CN$$

**Sol 7: (C)** Compound with $CH_3-\overset{O}{\overset{\|}{C}}-$ or $CH_3$–CH(OH)– group gives haloform reaction but this reaction is given only by aldehydes, ketones and alcohols, so acetic acid does not give haloform reaction. However acetic acid has three $\alpha$-H, therefore, statement-I is true but statement-II is false.

**Sol 8: (D)** p-hydroxy benzoic acid has higher boiling point than o-hydroxy benzoic acid because former prefers intermolecular H-bonding while the later prefer intramolecular H-bonding.



Intermolecular H-bonding



Intermolecular H-bonding

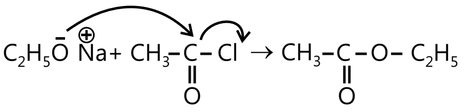
**Sol 9:** Saponification is hydrolysis of ester in presence of dilute base rather in presence of dilute acid.

**Sol 10:** Propanoic acid has higher boiling point than n-butanol because of more exhaustive H-bonding in former case.

**Sol 11: (D)** Esterification reaction is involved

$$CH_3COOH(\ell)+C_2H_5OH(\ell)\xrightarrow{H^+}CH_3COOC_2H_5(\ell)+H_2O(\ell)$$

**Sol 12: (C)**



$$C_2H_5\overset{-}{O}\overset{\oplus}{Na}+CH_3-\underset{O}{\underset{\|}{C}}-Cl\rightarrow CH_3-\underset{O}{\underset{\|}{C}}-O-C_2H_5$$

Ethyl ethanoate

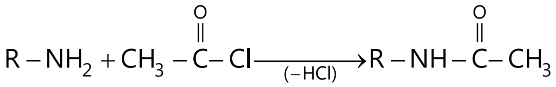
**Sol 13: (B)** Electron releasing groups (Alkyl groups) de stabilizes conjugate base.

The +I effect of $C_3H_7$ is less than - I effect of Cl

$K_a$ of $HC_3CH_2CH_2\underset{Cl}{\underset{|}{C}}H-COOH$ is $139\times10^{-5}$

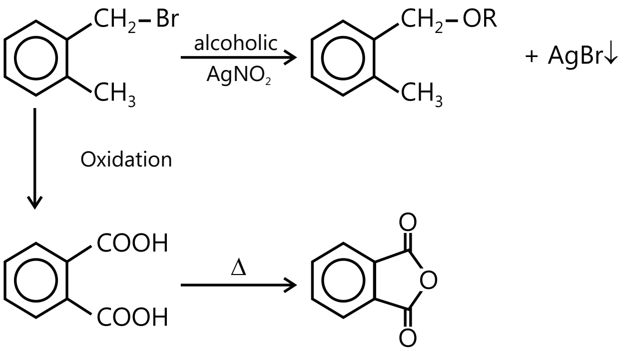
**Sol 14: (C)** Phenol gives violet colored complex compound with neutral $FeCl_3$, benzoic acid gives pale dull yellow ppt. with neutral $FeCl_3$

**Sol 15: (C)** By reaction with one mole of $CH_3-\overset{O}{\overset{\|}{C}}-Cl$ with one $-NH_2$ group the molecular mass increases with 42 unit. Since the mass increases by (390-180) = 210 hence the number of $-NH_2$ groups is 5.



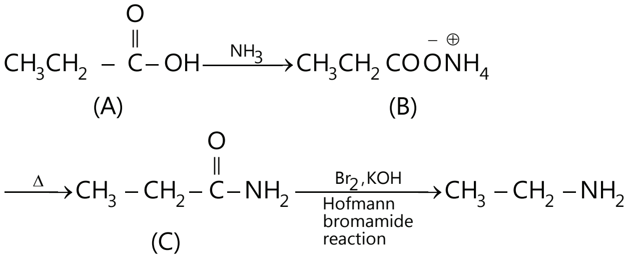
$$R-NH_2+CH_3-\overset{O}{\overset{\|}{C}}-Cl\xrightarrow[(-HCl)]{}R-NH-\overset{O}{\overset{\|}{C}}-CH_3$$

**Sol 16: (D)**



(Phthalic anhydride)

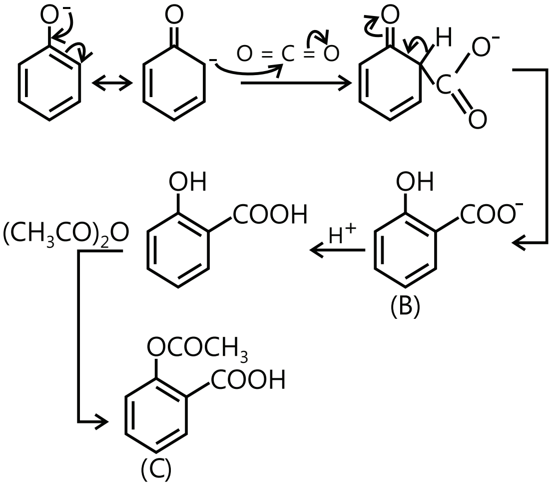
**Sol 17: (D)**



$$\underset{(A)}{CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH}\xrightarrow{NH_3}\underset{(B)}{CH_3CH_2\,CO\overset{-}{O}\overset{\oplus}{N}H_4}$$

$$\xrightarrow{\Delta}\underset{(C)}{CH_3-CH_2-\overset{O}{\overset{\|}{C}}-NH_2}\xrightarrow[\text{Hofmann bromamide reaction}]{Br_2,KOH}CH_3-CH_2-NH_2$$

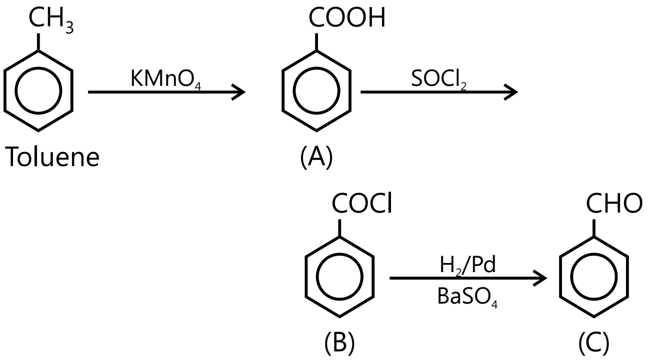
**Sol 18: (A)**



**Sol 19: (C)**

$$\begin{tikzcd} CH_3COOH \arrow[r, "LiAlH_4"] & CH_3CH_2OH \text{ 'A'} \arrow[d, "PCl_5"] \\ & CH_3CH_2Cl \text{ 'B'} \arrow[d, "Alc.KOH"] \\ & CH_2=CH_2 \text{ 'C'} \end{tikzcd}$$

**Sol 20: (D)**



**Sol 21: (C)** Hofmann bromamide degradation reaction

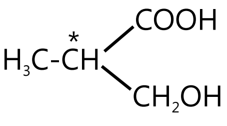
$$R-\overset{\overset{O}{\parallel}}{C}-NH_2+Br_2+4NaOH \longrightarrow$$
$$R-NH_2+Na_2CO_3+2NaBr+2H_2O$$

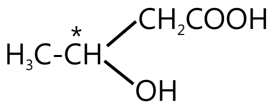
1 mole bromine and 4 moles of NaOH are used for per mole of amine produced.

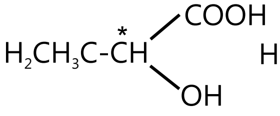
# JEE Advanced/Boards

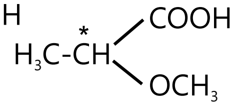
## Exercise 1

**Sol 1:** (i) The isomers have 1°of unsaturation that must be due to –COOH, since $CO_2$ is evolved on adding $NaHCO_3$. The remaining oxygen may be present as –OH or –OR.

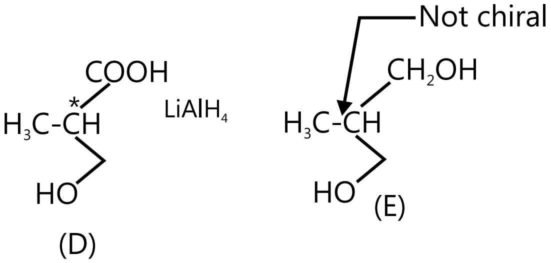

(D)


(E)


(F)

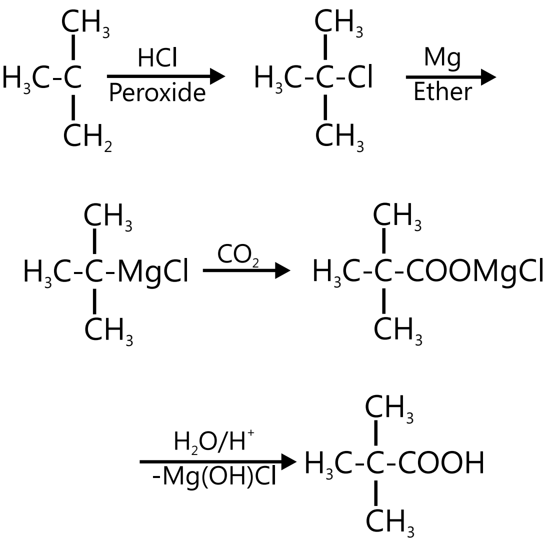

(G)

(ii) $LiAlH_4$ converts–COOH to $–CH_2OH$. Only (D) is reduced to an a chiral product.



(iii) The ether (G) differs from (E) and (F) in that it is inert to oxidation by $KMnO_4$ or $CrO_3$. (E) gives a positive iodoform test.

**Sol 2**:

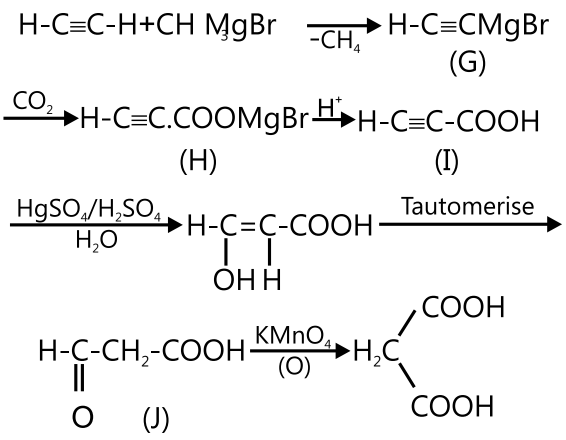


$$H_3C-\underset{\underset{CH_2}{|}}{\overset{\overset{CH_3}{|}}{C}} \xrightarrow[\text{Peroxide}]{HCl} H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl \xrightarrow[\text{Ether}]{Mg}$$

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-MgCl \xrightarrow{CO_2} H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-COOMgCl$$

$$\xrightarrow[-Mg(OH)Cl]{H_2O/H^+} H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-COOH$$

**Sol 3:**



$H\text{-}C\equiv C\text{-}H + CH_3MgBr \xrightarrow[-CH_4]{} H\text{-}C\equiv CMgBr$ (G)

$\xrightarrow{CO_2} H\text{-}C\equiv C.COOMgBr \xrightarrow{H^+} H\text{-}C\equiv C\text{-}COOH$

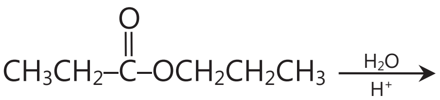
(H) (I)

$\xrightarrow[H_2O]{HgSO_4/H_2SO_4} H\text{-}\underset{OH}{C}=\underset{H}{C}\text{-}COOH \xrightarrow{\text{Tautomerise}}$

$H\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_2\text{-}COOH \xrightarrow[(O)]{KMnO_4} H_2C(COOH)_2$

(J)

**Sol 4:**



$CH_3CH_2\text{–}\overset{O}{\overset{\|}{C}}\text{–}OCH_2CH_2CH_3 \xrightarrow[H^+]{H_2O}$

$CH_3CH_2COOH + CH_3CH_2CH_2OH$

(A) (B)

$CH_3CH_2CH_2OHCH_3 \xrightarrow[(O)]{\text{Chromic acid}}$

$CH_2CHO \xrightarrow{(O)} CH_3CH_2COOH$

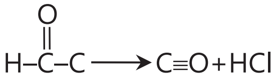
(A)

**Sol 5:** $RCO_2H \xrightarrow{SOCl_2} RCOCl \xrightarrow{NaN_3}$

$RCON_3 \xrightarrow{D} RNCO \xrightarrow{\text{Hydrolysis}} RNH_2$

**Sol 6:** $C\equiv O$ bond is very stable due to large $\Delta H_f$ of CO;

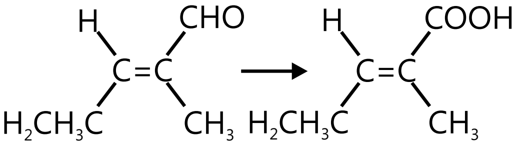
so the decomposition reaction



$H\text{–}\overset{O}{\overset{\|}{C}}\text{–}C \longrightarrow C\equiv O + HCl$

is favoured. Formyl chloride is not stable above –60°C.

**Sol 7:** An extremely mild but selective oxidizing agent for aldhydes is silver oxide suspended in aqueous base. An unsaturated acid is obtained with this reagent because the >C=C<remains untouched by this reagent.

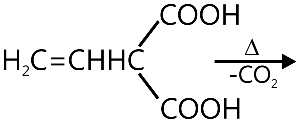


**Sol 8:**

$C_5H_6O_4 \xrightarrow[-CO_2]{\Delta} C_4H_6O_2 \xrightarrow{H_2O}$

(B)

$CH_3CH_2CH_2COOH$



$CH_2=CH\text{-}HC_2COOH \xrightarrow{H_2/Ni} CH_3CH_2CH_2COOH$

(B)

**Sol 9:**

| | |
|---|---|
| (A) $(CH_3CO)_2O$ | (B) $CH_3COOH$ |
| (C) $CH_3COOC_2H_5$ | (D) $C_2H_5OH$ |
| (E) $CH_3COCH_3$ | |

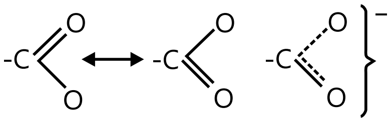
**Sol 10:** (A) $(C_2H_5COOC_2H5)$

(B) $C_2H_5CO\text{–}CH(CH_3)COOC_2H_5$

(C) $C_2H_5COCH(CH_3)COOH$

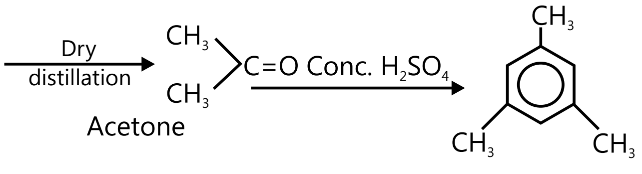
**Sol 11:** An alkali salt of palmitic acid is known as soap. The general formula of palmitic acid $C_{15}H_{31}COOH$. Which on hydrolysis in presence of alkali give soap($C_{15}H_{31}COONa$) and glycerol as by product.

**Sol 12:** Acid do not reacts with $NaHSO_3$though they have >C=O group because of resonance stabilization. The resonance take place as follows.



**Sol 13:** $CH_3COOH \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca$

| (X) | (Y) |
|---|---|
| Acetic acid | Cal. acetate |

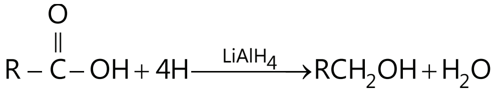


(Z) Mesitylene

**Sol 14:** $CH_3CH_2COOH \xrightarrow[SeO_2]{[O]} CH_3CO\,COOH + H_2O$

Propionic acid  Pyruvic acid

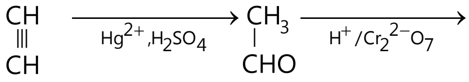
**Sol 15:** Acid are directly reduced to the corresponding primary alcohol with powerful reactant like $LiAlH_4$. It attack only on the carbonyl group of a fatty acid.



$$R-\overset{\overset{\large O}{||}}{C}-OH + 4H \xrightarrow{LiAlH_4} RCH_2OH + H_2O$$

Alkanol

**Sol 16:**



$$CH{\equiv}CH \xrightarrow{Hg^{2+}, H_2SO_4} \underset{\underset{\large CHO}{|}}{CH_3} \xrightarrow{H^+/Cr_2{}^{2-}O_7}$$

$CH_3COOH \xrightarrow[CaO]{NaOH} CH_4$

**Sol 17**: $CH_3CN \xrightarrow{H_3O^+} CH_3COOH \xrightarrow{NH_3}$

Ethane nitrile  Ethanoic acid

(X)  (Y)

$CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2$

Ammonium ethanoate  Ethanamide

$\xrightarrow{Br_2/KOH} CH_3NH_2$

Amino methane

**Sol 18:** $CH_3COONa \xleftarrow{NaOH} CH_3COOH$

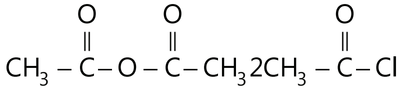
(Z)  (X)

$\xrightarrow{PCl_3} CH_3COCl$

(Y)

$CH_3COCl + CH_3COONa \rightarrow$

(Y)  (Z)



$$CH_3-\overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-CH_32CH_3-\overset{\overset{O}{||}}{C}-Cl$$

(E)  (Y)

**Sol 19:** (i) $CH_3Cl \rightarrow CH_3COCl$

Methyl chloride Acetyl chloride

$CH_3Cl \xrightarrow{Mg} CH_3MgCl \xrightarrow[H_2O/H^+]{CO_2}$

Methyl chloride

$CH_3COOH \xrightarrow{SOCl_2} CH_3COCl$

Acetyl chloride

(ii) $C_2H_5OH \longrightarrow CH_3CONH_2$

Ethyl alcohol  Acetamide

$CH_3OH \xrightarrow[K_2Cr_2O_7/H^+]{[O]} CH_3CHO \xrightarrow{[O]}$

Methyl alcohol

$CH_3COOH \xrightarrow{SOCl_2} CH_3COCl$

$\xrightarrow{NH_2} CH_3CONH_2$ Acetamide

(iii) $CH_3COOH \longrightarrow CH_3COOC_2H_5$

Acetic acid  Ethyl acetate

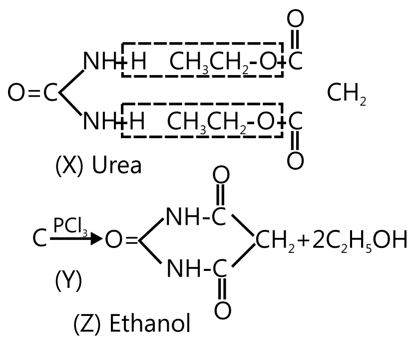
$CH_3COOH \xrightarrow{LiAlH} CH_3CH_2OH$

Acetic acid

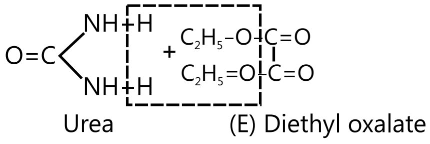
$\xrightarrow{CH_3COOH/H^+} CH_3COOC_2H_5$

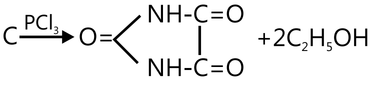
Ethyl acetate

**Sol 20:** (i)



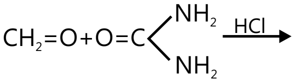
(ii)





(F) Parabanic acid
(Oxalyl urea)

(iii)



$$CH_2{=}O + O{=}C\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix} \xrightarrow{HCl}$$

Formaldehyde (X) Urea

$CH_2\text{-}(OH)\text{-}NH\text{-}CONH_2 \xrightarrow{CH_2=O}$

Monomethylol urea

$CH_2(OH)NHCONH(OH)CH_2 \xrightarrow[Resin]{Urea}$

Dimethylol urea
urea-formaldehyde

**Sol 21:** (i)

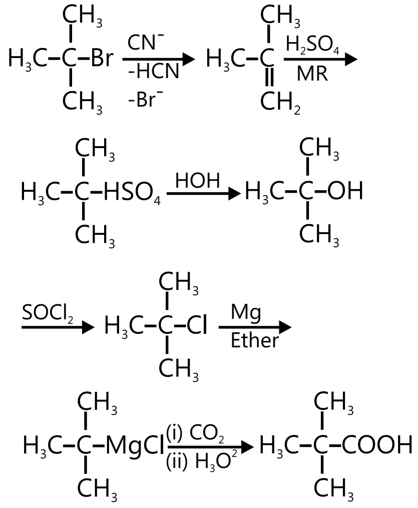
$CH_3CH_2CH_2CH_2Br \xrightarrow{CN^-}$

$CH_3CH_2CH_2CH_2CN \xrightarrow{-Br^- / 2HOH/H^+}$

$CH_3CH_2CH_2CH_2COOH$

n – Pentanoic acid

(ii)



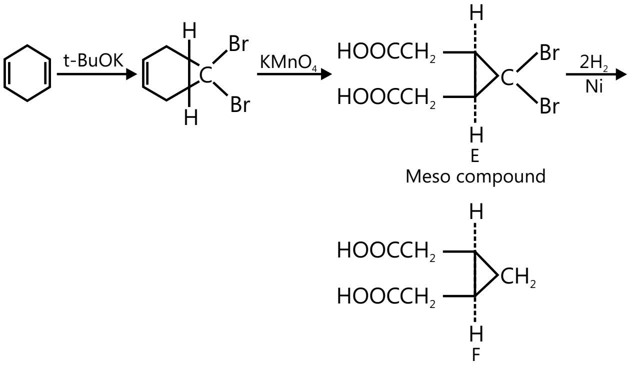
$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-Br \xrightarrow[\text{-HCN, -Br}^-]{CN^-} H_3C-\overset{CH_3}{\underset{CH_2}{C}} \xrightarrow[MR]{H_2SO_4}$$

$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-HSO_4 \xrightarrow{HOH} H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH$$

$$\xrightarrow{SOCl_2} H_3C-\overset{CH_3}{\underset{CH_3}{C}}-Cl \xrightarrow[Ether]{Mg}$$

$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-MgCl \xrightarrow[(ii)\ H_3O^2]{(i)\ CO_2} H_3C-\overset{CH_3}{\underset{CH_3}{C}}-COOH$$

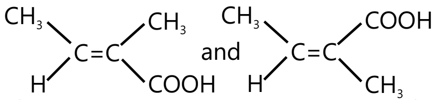
**Sol 22:**



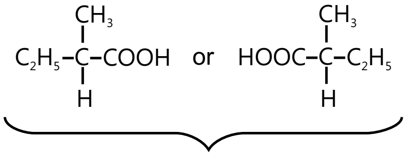
E
Meso compound

F
Meso compound

**Sol 23:**



(A) Geometrical isomers



$$C_2H_5-\overset{CH_3}{\underset{H}{C}}-COOH \text{ or } HOOC-\overset{CH_3}{\underset{H}{C}}-C_2H_5$$

(B)

**Sol 24:** (A) $CH_3CHOHCH_2COOH$

(B) $CH_3CH=CHCOOH$

(C) $CH_3CH=CHCOCl$

(D) $CH_3-CH=HCON(CH_3)_2$

(E) $CH_3COCH_2COOH$

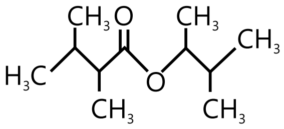
(F) $CH_3COCH_3$

(G) $CH_3CH_2CH_3$

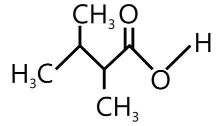
**Sol 25:** Is a saturated monoester with

M.W = 186

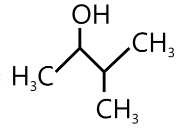
F =



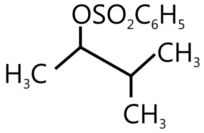
G =



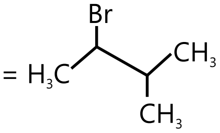
H =



J =

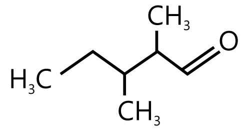


K =

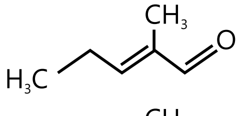


**Sol 26:**

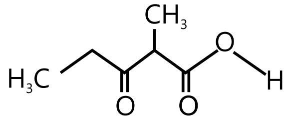
A =



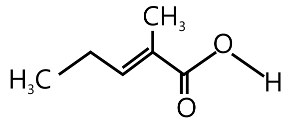
B =

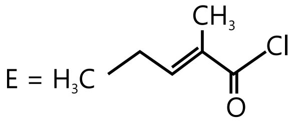


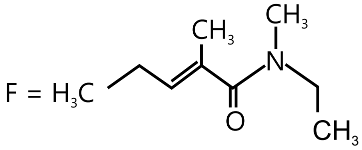
C =



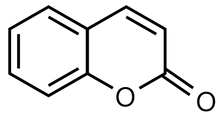
D =

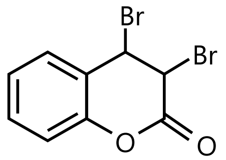


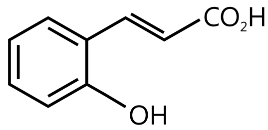
E =


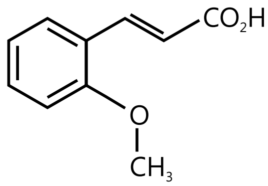
F =


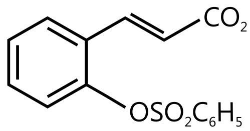
**Sol 27:**

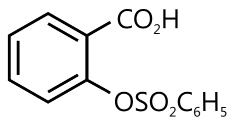
A =


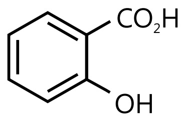
B =


C =


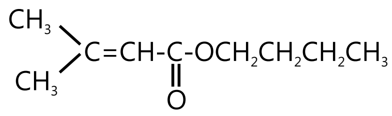
D =


E =


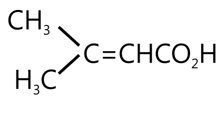
F =


G =


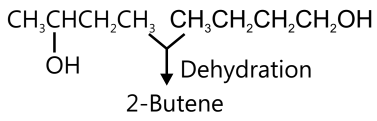
**Sol 28:**

(A)


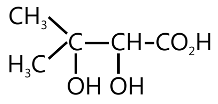
$$(CH_3)_2C{=}CH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OCH_2CH_2CH_2CH_3$$

(B)


$$(CH_3)_2C{=}CHCO_2H$$

(C)


$$\underset{\displaystyle OH}{CH_3\underset{|}{C}HCH_2CH_3} \quad CH_3CH_2CH_2CH_2OH \xrightarrow{\text{Dehydration}} \text{2-Butene}$$

(D)


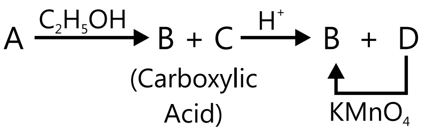
$$(CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}CO_2H$$

M.F $C_5H_{10}O_4$

(E) $O{=}CH{-}CO_2H$

M.F $C_2H_2O_3$

**Sol 29:** The given reaction are as follows.



$$A \xrightarrow{C_2H_5OH} B + C \xrightarrow{H^+} B + D$$

$$\underset{O}{B} \xrightarrow[D]{Ca(OH)_2} \underset{(E)}{C_3H_6}$$

The compound E must be ketonic compound as it does not give Tollens test and does not reduce Fehling's solution but forms a 2, 4-dinitrophenyl-hydrazone. Therefore, its structure would be $CH_3COCH_3$(acetone).

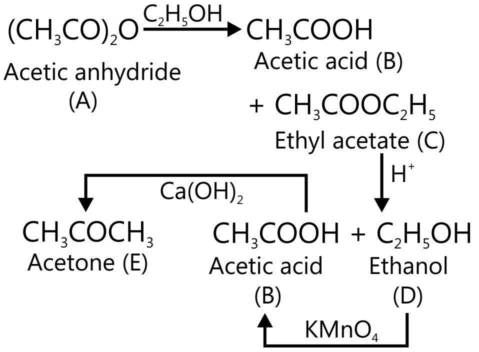
Since E is obtained by heating B with $Ca(OH)_2$, the compound B must be $CH_3COOH$ (acetic acid).

Since B is obtained by oxidation of D with $KMnO_4$, the compound D must an alcohol with molecular formula $CH_3CH_2OH$(ethanol).

Since B and D are obtained by acid hydrolysis of C, the compound C must be an ester $CH_3COOC_2H_5$(ethyl acetate).

Since the compounds B (acetic acid) and C (ethyl acetate) are obtained by treating A with ethanol, the compound A must be an anhydride $(CH_3CO)_2O$ (acetic anhydride).

The given reaction are



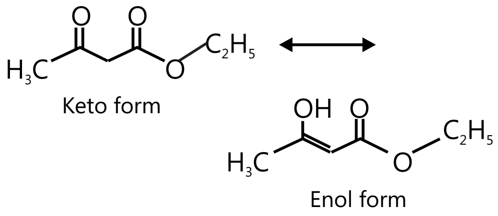
$$\underset{\text{Acetic anhydride (A)}}{(CH_3CO)_2O} \xrightarrow{C_2H_5OH} \underset{\text{Acetic acid (B)}}{CH_3COOH} + \underset{\text{Ethyl acetate (C)}}{CH_3COOC_2H_5}$$

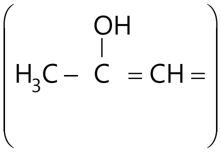
$$\underset{\text{Ethyl acetate (C)}}{CH_3COOC_2H_5} \xrightarrow{H^+} \underset{\text{Acetic acid (B)}}{CH_3COOH} + \underset{\text{Ethanol (D)}}{C_2H_5OH}$$

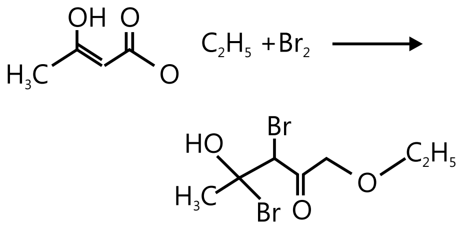
$$\underset{\text{Acetic acid (B)}}{CH_3COOH} \xrightarrow{Ca(OH)_2} \underset{\text{Acetone (E)}}{CH_3COCH_3}$$

$$\underset{\text{Ethanol (D)}}{C_2H_5OH} \xrightarrow{KMnO_4} \underset{\text{Acetic acid (B)}}{CH_3COOH}$$

**Sol 30:** Acetoacetic ester shows tautomerism and the two forms are called as keto and enol forms.



The enol  $\left(H_3C-\overset{OH}{\overset{|}{C}}=CH=\right)$ gives blue-violet colour with $FeCl_3$ solution. When $Br_2$ is added, it reacts at once with = of the enol form.

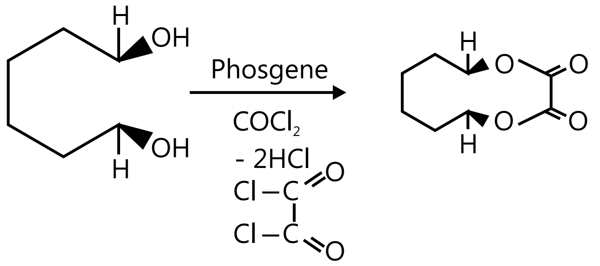


As soon as enol form is consumed, its colouration with $FeCl_3$ disappears and excess of bromine gives brown colour. As keto and enol forms are in equilibrium, when enol form is used, the equilibrium shifts to right hand side to give more enol form which discharges the colour of excess of $Br_2$ and gives blue violet colour with excess of $FeCl_3$ present in the reaction mixture.

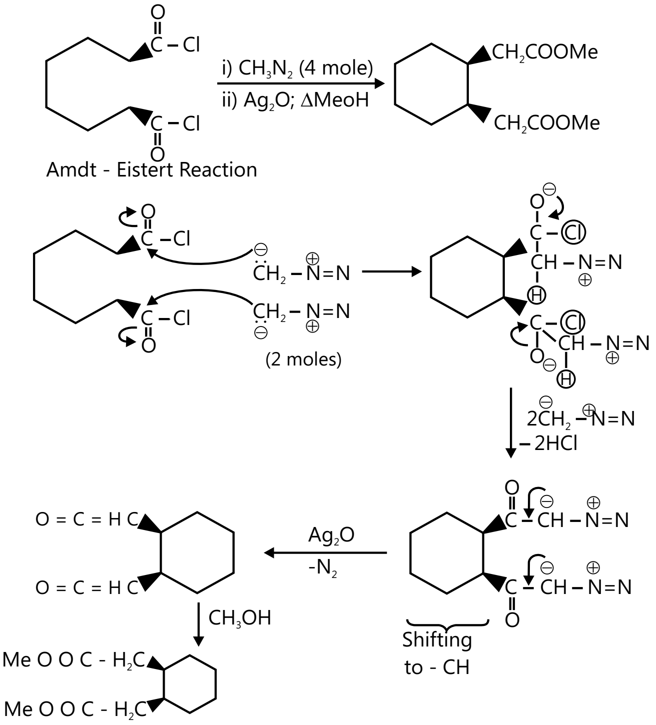
# Exercise 2

## Single Correct Choice Type

**Sol 1: (D)**

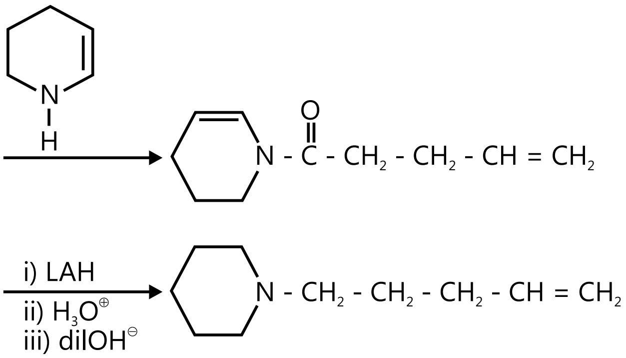


**Sol 2: (B)**

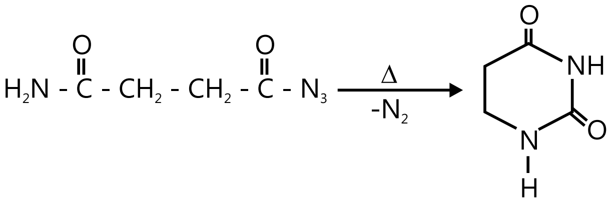


**Sol 3: (B)**

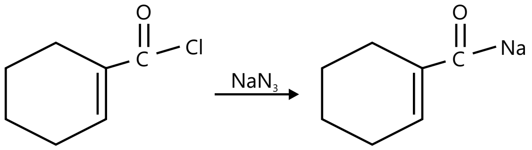
$$HOOC-CH_2-CH_2-CH=CH_2 \xrightarrow{SOCl_2}$$
$$ClOC-CH_2-CH_2-CH=CH_2$$



**Sol 4: (C)**



**Sol 5: (B)**



### Multiple Correct Choice Type

**Sol 6: (A, C, D)** Self–explanatory, Rearrangement reactions

**Sol 7: (A, C)** Self-explanatory

### Assertion Reasoning Type

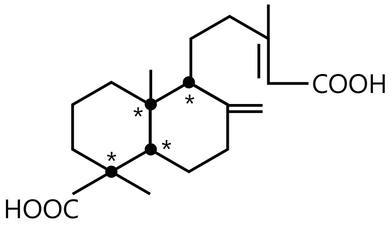
**Sol 8: (D)** The given compound is optically active.

### Comprehension Type

**Paragraph 1 (Questions 9 to 12)**

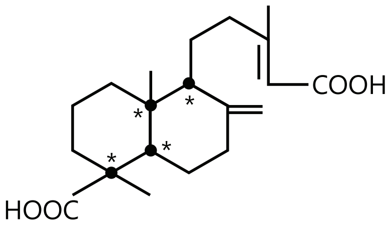
**Sol 9: (A)** Abstraction of $\alpha$ -H takes place to given a carbanion, from the lower side to give $C_2OH_{38}$

**Sol 10: (C)** Agathene Dicarboxylic Acid:



$\therefore$ 4 Chiral Carbons (shown by *)

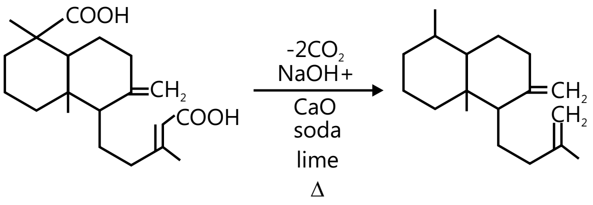
**Sol 11: (C)** No. of Chiral carbons = 4.



$\therefore$ No. of Optical isomers = $2^4 = 16$

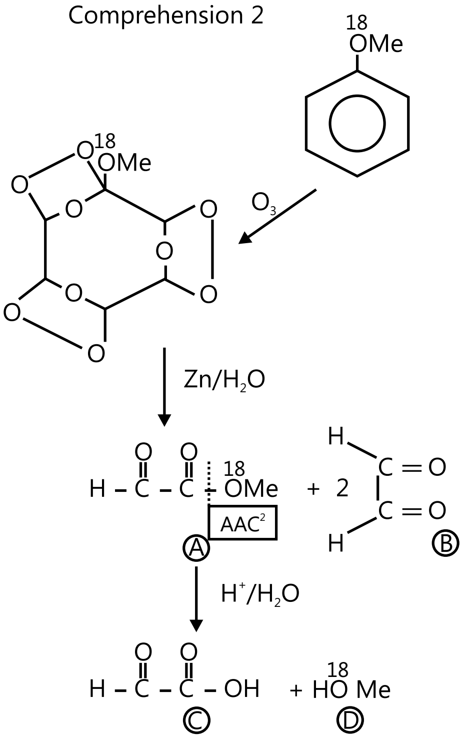
$\therefore$ Stereoisomers = No. of optical isomers + No. of geometrical isomers = 32.

**Sol 12: (A)**



**Paragraph 2 (Questions 13 to 15)**

**Sol 13: (C); Sol 14: (A); Sol 15: (D)**

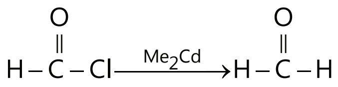


**Paragraph 3 (Qeustions 16 to 18)**

**Sol 16: (A)** Mechanism of formation of A and B is $A_{AC}^{2}$

**Sol 17: (D)** Both B and C are redox reaction as B involves reduction and C reaction involves oxidation step.

**Sol 18: (B)**



$$H-\overset{O}{\overset{\|}{C}}-Cl\xrightarrow{Me_2Cd}H-\overset{O}{\overset{\|}{C}}-H$$

### Match the Columns

**Sol 19:** A → s; B → p; C → r; D → s

(A) It is an example of Dieckmann reaction which involves condensation of two ester.

(B) Condensation between an active methylene compound and an keto compound is known as Knoevenagel reaction.

(C) It is an example of reformatsky reaction

(D) It is also an example of Dieckmann reaction which involves condensation of two ester to form a ring structure.

**Q.20** A → p; B → q, s; C → r.

(A) $CH_3-CH=CH_2 \xrightarrow[Zn]{O_3} (U)+(V)$ –Haloform rection

(B) Product are ketone and aldehyde which can be differentiated by Fehling's and Tollens reagent.

(C) Product are acid and alcohol. Acid gives effervescence with aq. $NaHCO_3$.

**Q.21** A → p; B → r, t; C → p, s; D → p, q, s

(A) Markonikov's rule-Regioselective

(B) Example of Diels Alder reaction-Cyclic addition, stereospecific

(C)Addition reaction- Regioselective

And will form diastereomers.

(D) Regio as well as stereoselective addition and will form diastereomers.

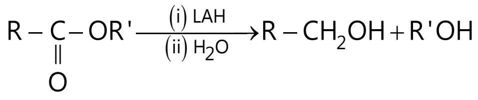
**Q.22** A → q, r; B → p, q; C → r, s

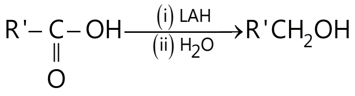
(A) Acid will give brisk effervescence with $NaHCO_3$. Other organic product formed will give haloform test

(B) Presence of unsaturation will cause decolourisation of $Br_2$ water. And Acid functional group will give effervescence with $NaHCO_3$.

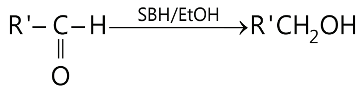
(C) One of the organic product formed will give haloform test. One of the organic product formed will give 2, 4 DNP

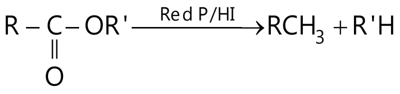
**Q.23** A → q ; B → r; C → p; D → r; E → s, t

(A)

$$R-\underset{\underset{O}{\|}}{C}-OR' \xrightarrow[(ii)\ H_2O]{(i)\ LAH} R-CH_2OH+R'OH$$

(B)

$$R'-\underset{\underset{O}{\|}}{C}-OH \xrightarrow[(ii)\ H_2O]{(i)\ LAH} R'CH_2OH$$

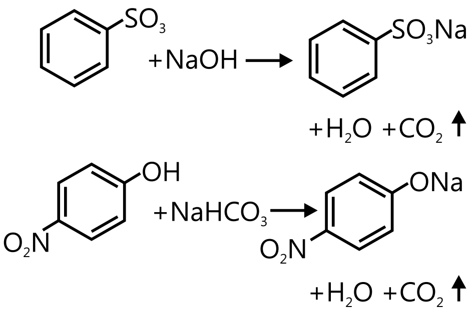
(C) $R'-CH_2-Br \xrightarrow{LAH} R'CH_3$

(D)

$$R'-\underset{\underset{O}{\|}}{C}-H \xrightarrow{SBH/EtOH} R'CH_2OH$$

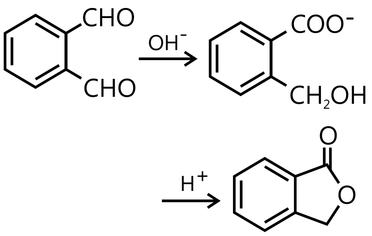
(E)

$$R-\underset{\underset{O}{\|}}{C}-OR' \xrightarrow{Red\ P/HI} RCH_3+R'H$$

## Previous Years' Questions

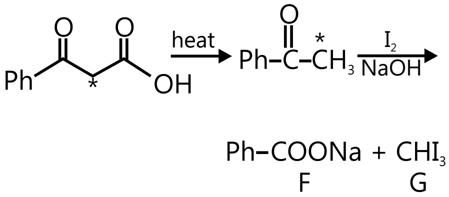
**Sol 1: (D)**



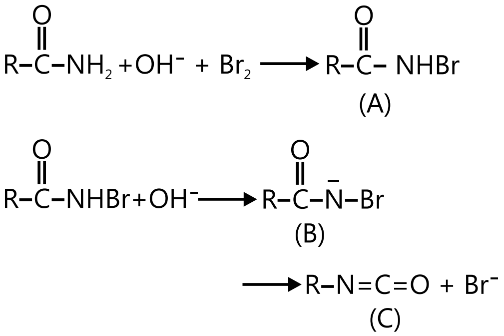
**Sol 2: (C)**



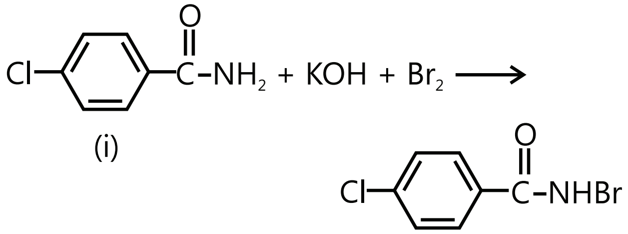
**Sol 3: (C)**



**Sol 4; (A, C)**

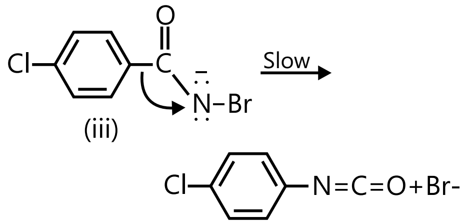

$$R-\overset{\overset{O}{\|}}{C}-NH_2+OH^- + Br_2 \longrightarrow R-\overset{\overset{O}{\|}}{C}-NHBr$$
(A)
$$R-\overset{\overset{O}{\|}}{C}-NHBr+OH^- \longrightarrow R-\overset{\overset{O}{\|}}{C}-\overset{-}{N}-Br$$
(B)
$$\longrightarrow R-N=C=O + Br^-$$
(C)

**Sol 5: (D)**



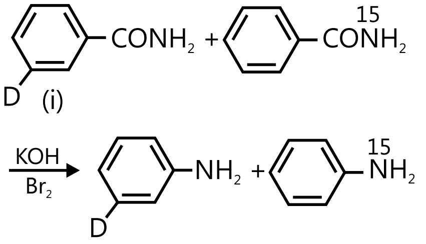
An intermediate (ii)

**Sol 6: (D)**

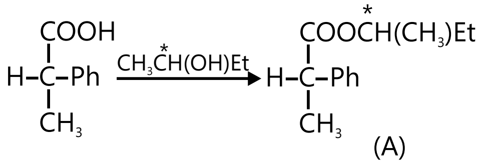


(iv)

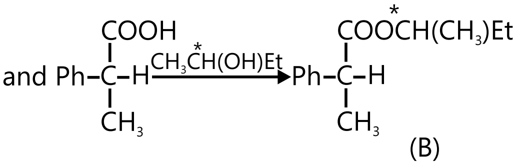
**Sol 7: (B)** The rate determining step of Hofmann bromide reaction is unimolecular rearrangement of bromamide anion (iii) and no cross-products are formed when mixture of amides are taken.



**Sol 8:** The two stereoisomers of 2-phenyl propanoic acid in the racemic mixture are :



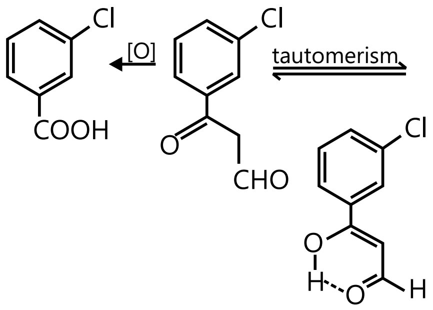
(A)



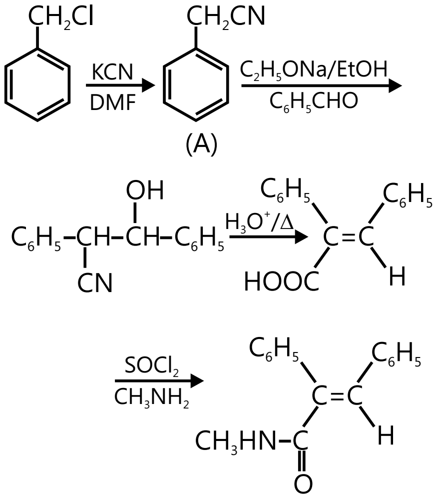
(B)

Here A and B are diastereomers.

**Sol 9:** Compound A of molecular formula $C_9H_7O_2Cl$ exist in keto and predominantly in enolic from B. Hence, A must be a carbonyl compound which contain $\alpha$-H. Enolic forms of B predominates because of presence of intramolecular H-bonding.



**Sol 10:**



**Sol 11: (A); Sol 12: (C)**

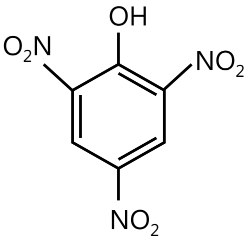
$$CH_3-CH_2-C\equiv C-CH_2-CH_2Br\xrightarrow[3.H_3O^+]{1.Mg/Ether\ \ 2.CO_2}$$

$$J\xrightarrow{K}CH_3-CH_2-C\equiv C-CH_2-COCl_2$$

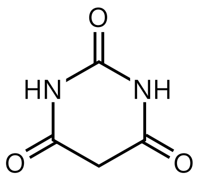
$J = CH_3-CH_2-C\equiv C-CH_2-COOH$

$K = SOCl_2$

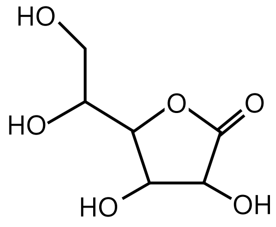
**Sol 13: (D)**



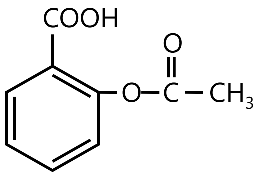
(Picric Acid)



(Barbituric Acid)

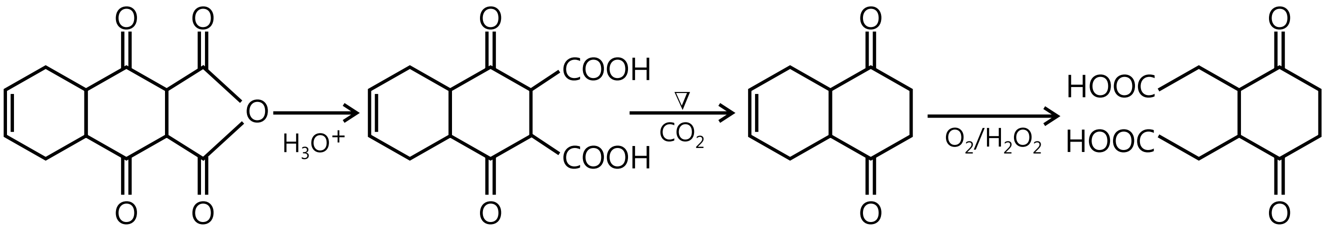


(Ascorbic Acid)

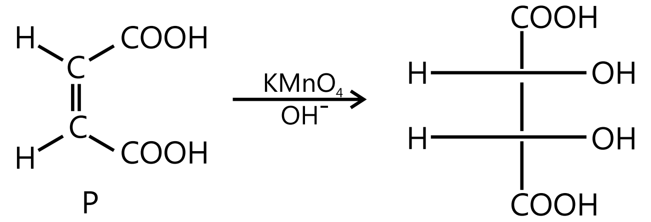


(Asprin)

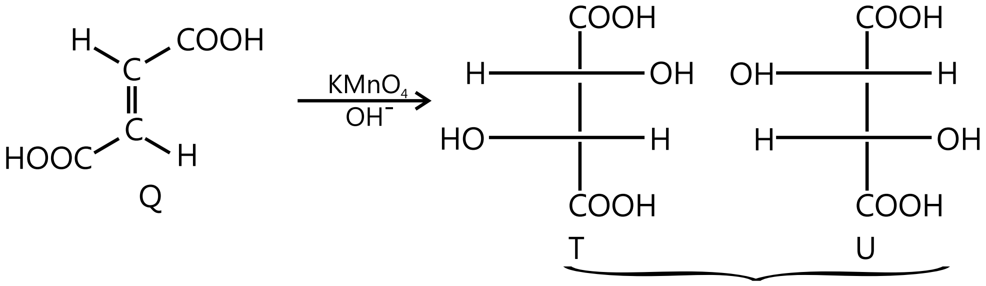
**Sol 14: (B)**



**Sol 15: (B)**

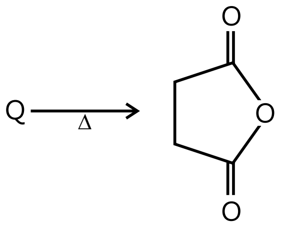


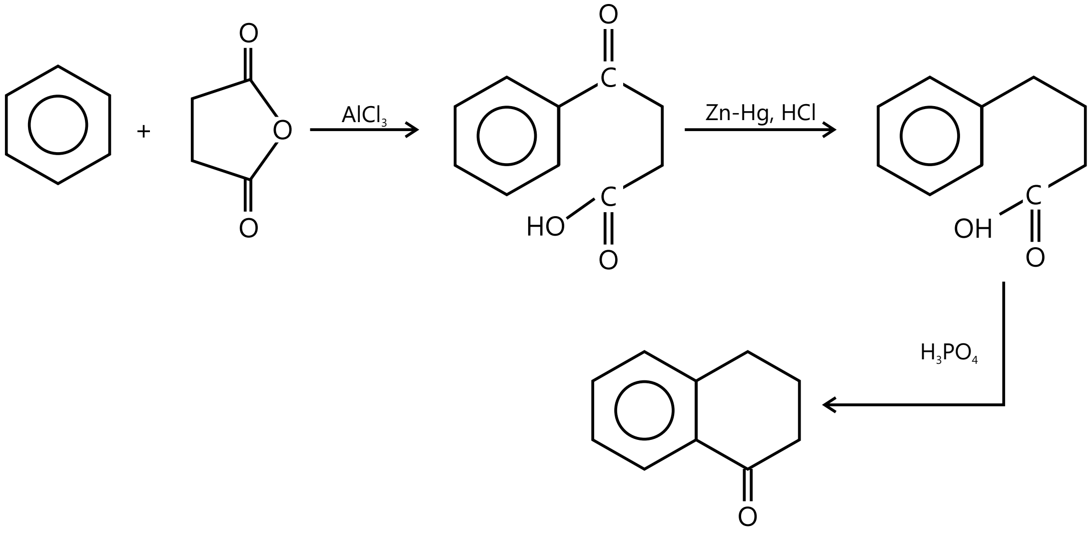
S→optically inactive



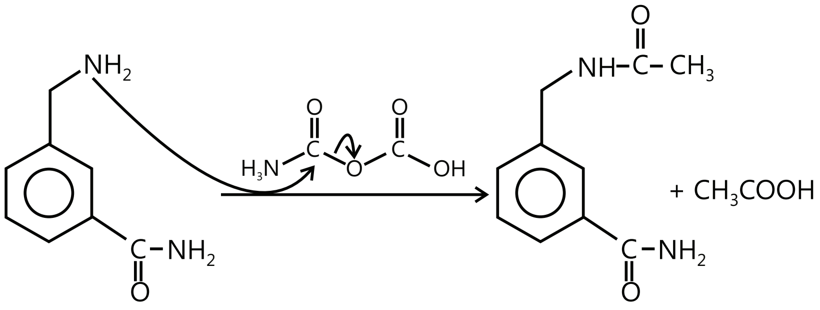
Optically inactive pair

**Sol 16: (A)**

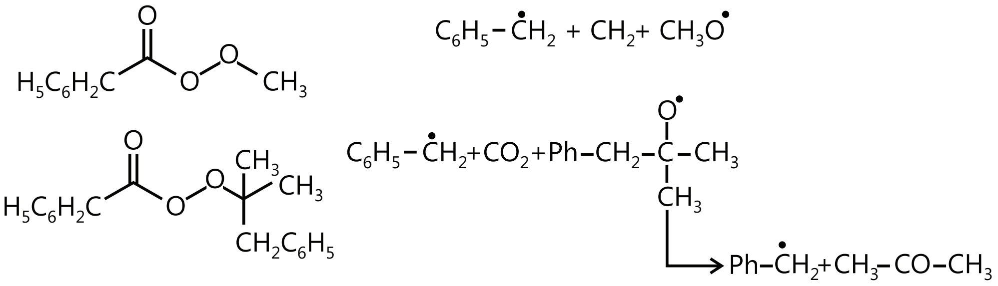


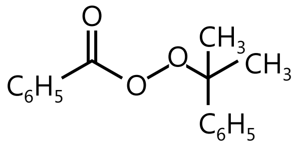


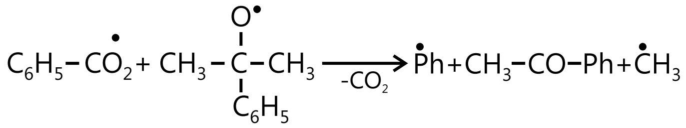
**Sol 17: (A)** Only amines undergo acetylation and not acid amides.



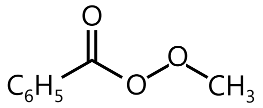
**Sol 18: (A)** (i) - p; (ii) - r; (iii) - s; (iv) - q

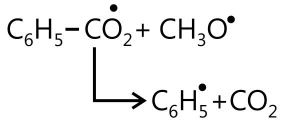






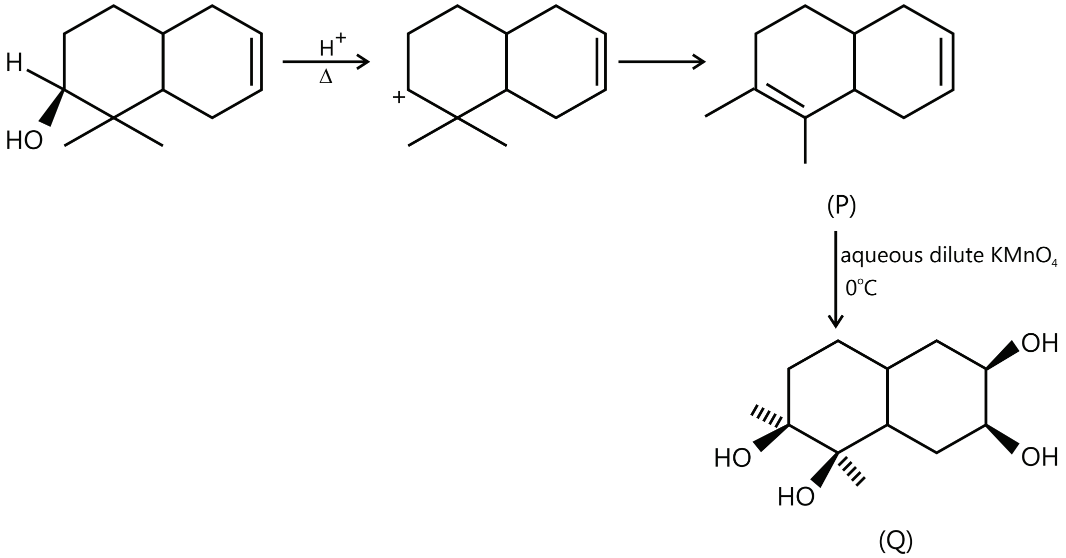
$$C_6H_5-\dot{C}O_2 + CH_3-\overset{O^{\bullet}}{\underset{C_6H_5}{C}}-CH_3 \xrightarrow[-CO_2]{} \dot{P}h + CH_3-CO-Ph + \dot{C}H_3$$





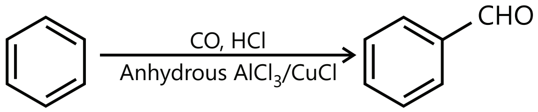
$$C_6H_5-\dot{C}O_2 + CH_3O^{\bullet}$$
$$\longrightarrow C_6\dot{H}_5 + CO_2$$

**Sol 19: (D)**

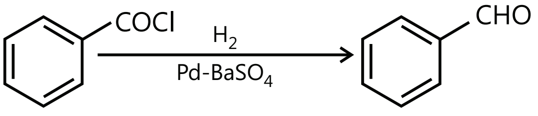


**Sol 20: (A, B, C, D)**

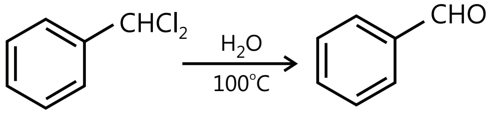
(I)



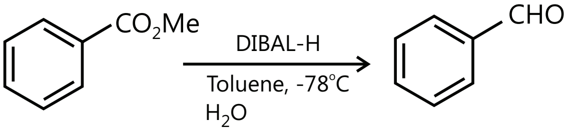
(III)



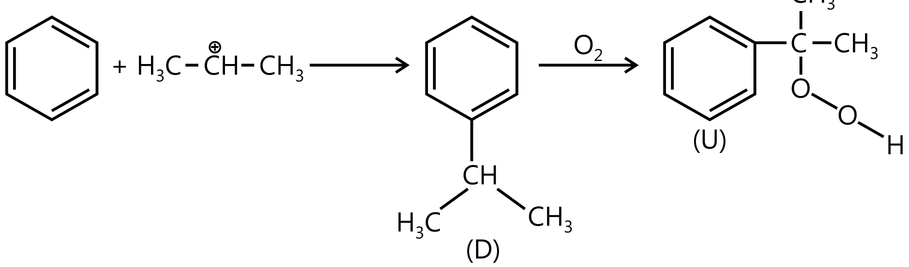
(II)



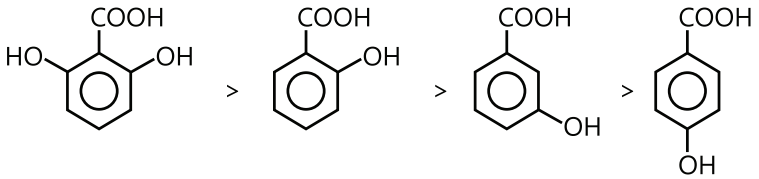
(IV)



**Sol 21: (B)**

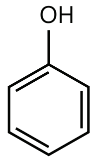


**Sol 22: (A)**



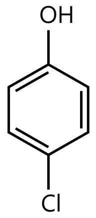
**Sol 23: (C)** $NaBH_4$ is a mild reducing agent. It selectively reduces aldehydic group.

**Sol 24: (A)**



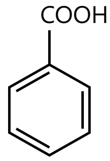
(I)

pKa=9.98



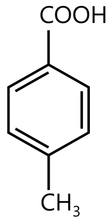
(II)

pKa=9.38



(III)

pKa=4.17

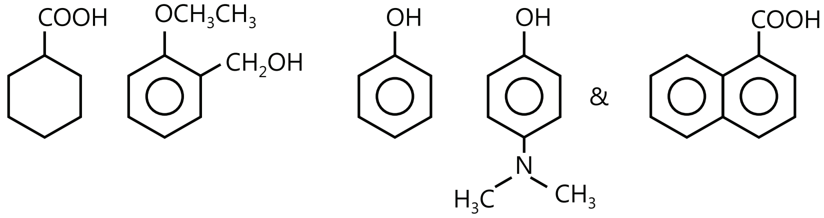


(IV)

pKa=4.37

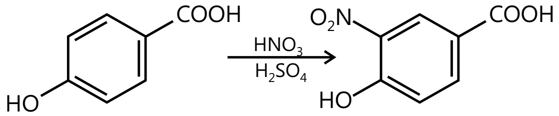
Decreasing order of acidic strength: III > IV > II > I

**Sol 25: (5)**



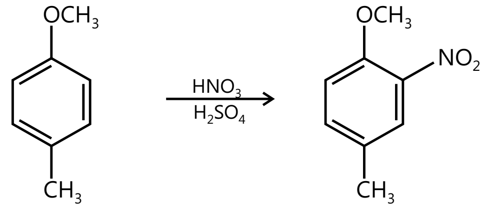
are soluble in aqueous NaOH.

**Sol 26: (C)**

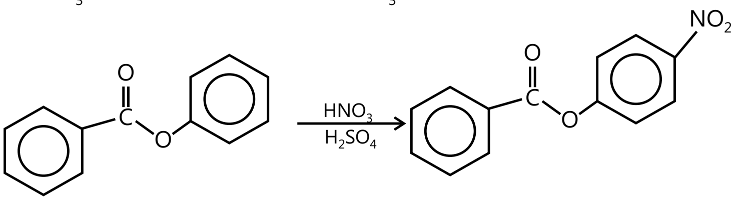


(P)

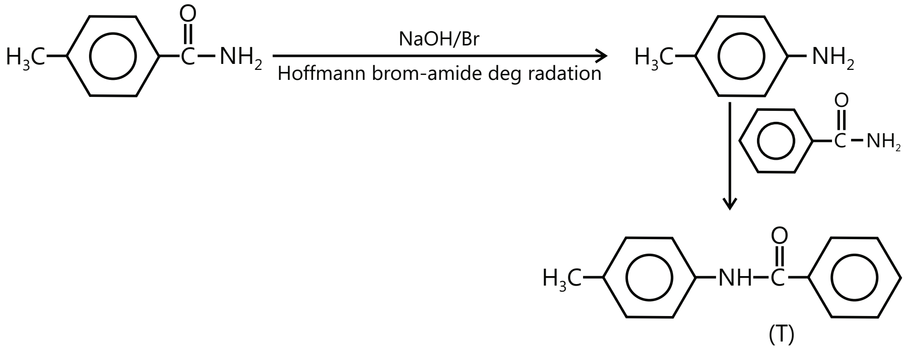
(-OH group is more activating)



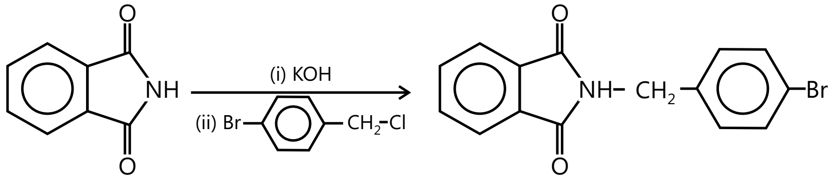
(-$OCH_3$ group is more activating)



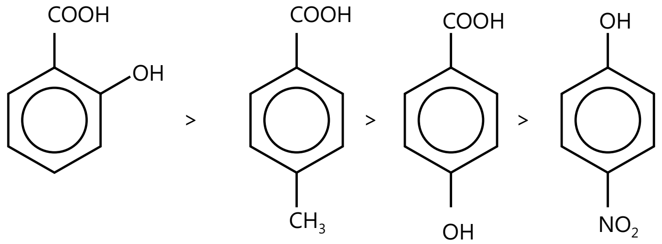
**Sol 27: (C)**



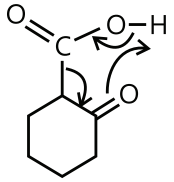
**Sol 28: (A)**



**Sol 29: (C)** Due to ortho effect o-hydroxy benzoic acid is strongest acid and correct order of decreasing $K_a$ is



**Sol 30: (B)** In decarboxylation, $\beta$-carbon acquire $\delta^-$ charge. Whenever $\delta^-$ charge is stabilized decarboxylation becomes simple. In (B) it is stabilized by-m and-o of C=O, which is best amongst the options offered.



**Sol 31: (A, C, D)**