Class 12

2017-18

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Carboxylic Acid and Derivatives

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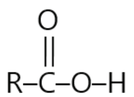
24. CARBOXYLIC ACID AND DERIVATIVES

1. INTRODUCTION

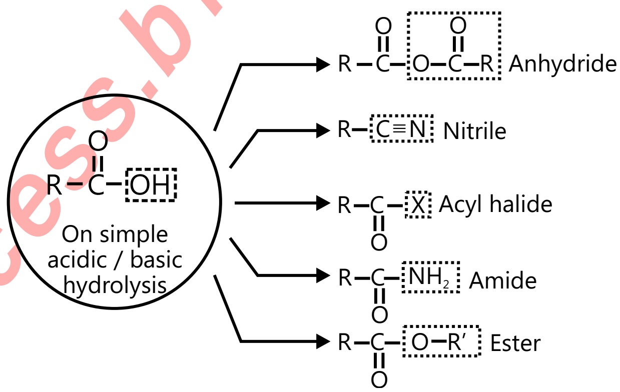
Compounds containing the carboxyl group are distinctly acidic and are called carboxylic acids.



Carboxylic Acid

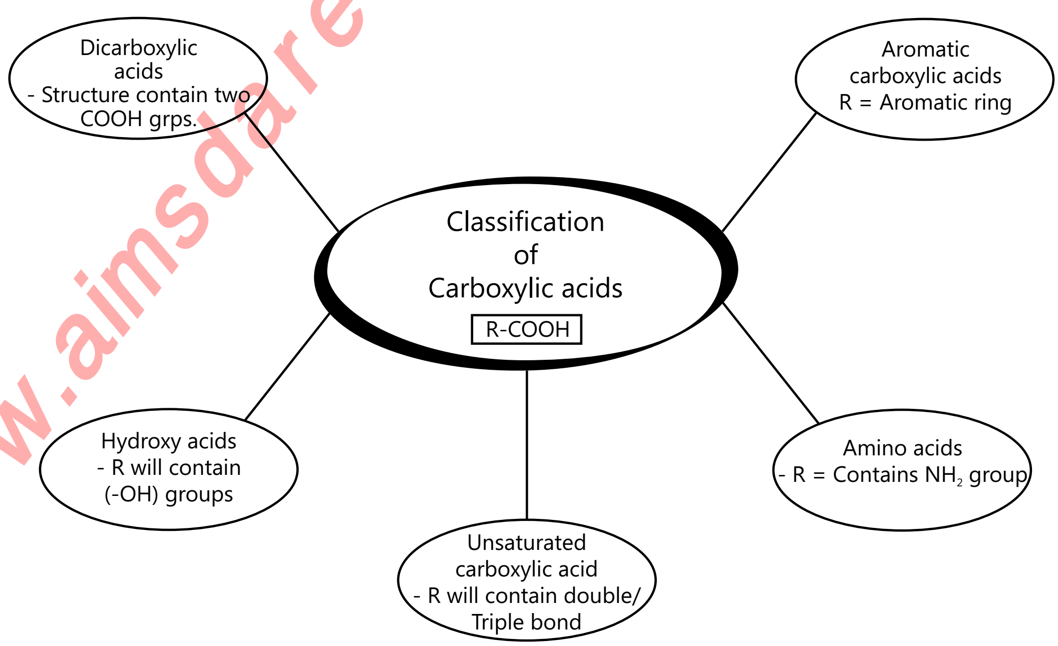
They have general formula $C_nH_{2n}O_2$

Carboxylic acid derivatives are compounds with functional groups that can be converted to carboxylic acids by a simple acidic or basic hydrolysis.



Flowchart 24.1: Derivatives of carboxylic acid

2. CLASSIFICATION OF CARBOXYLIC ACIDS



Flowchart 24.2: Classification of carboxylic acid

3. NOMENCLATURE OF CARBOXYLIC ACIDS

The IUPAC system of nomenclature assigns a characteristic suffix to these classes. The ending "e" is removed from the name of the parent chain and is replaced –"oic" acid.

Name → Alkan$\boxed{\text{e}}$ → Alkan$\boxed{\text{oic acid}}$

→ Given the # 1 location

Position in numbering.

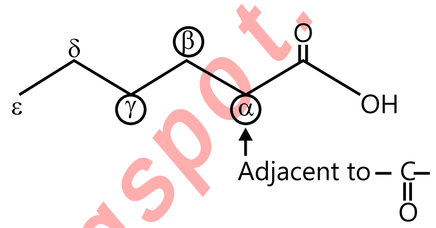
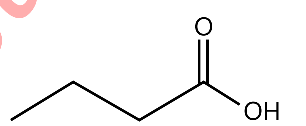


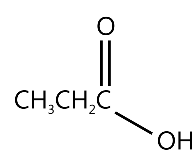
Table 24.1: IUPAC name of simple carboxylic acid

Formula	Common Name	Source	IUPAC Name	Melting Point	Boiling Point
HCOOH	Formic acid	Ants (L. Formica)	Methanoic acid	8.4 °C	101 °C
CH_3COOH	Acetic acid	Vinegar (L. Acetum)	Ethanoic acid	16.6 °C	118 °C
CH_3CH_2COOH	Propionic acid	Milk (Gk. Protus prion)	Propanoic acid	-20.8 °C	141 °C
$CH_3(CH_2)_2COOH$	Butyric acid	Butter (L. Butyrum)	Butanoic acid	-5.5 °C	164 °C
$CH_3(CH_2)_3COOH$	Valeric acid	Valerian root	Pentanoic acid	-34.5 °C	186 °C
$CH_3(CH_2)_4COOH$	Caproic acid	Goats (L. Caper)	Hexanoic acid	-4.0 °C	205 °C
$CH_3(CH_2)_5COOH$	Enanthic acid	Vines (Gk. Oenanthe)	Heptanoic acid	-7.5 °C	223 °C
$CH_3(CH_2)_6COOH$	Caprylic acid	Goats (L. Caper)	Octanoic acid	16.3 °C	239 °C
$CH_3(CH_2)_7COOH$	Pelargonic acid	Pelargonium (an herb)	Nonanoic acid	12.0 °C	253 °C
$CH_3(CH_2)_8COOH$	Capric acid	Goats (L. Caper)	Decanoic acid	31.0 °C	219 °C

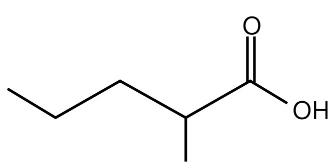
Example:



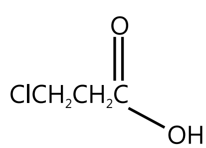
Butanoic acid
(Butyric Acid)



Propanoic acid
(Propionic Acid)

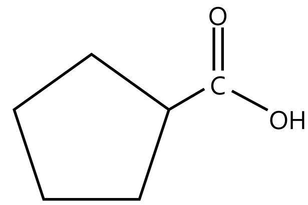
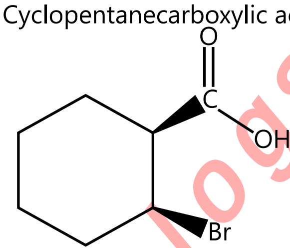
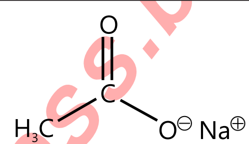
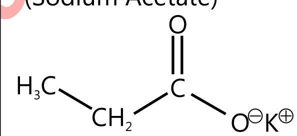
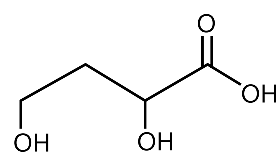
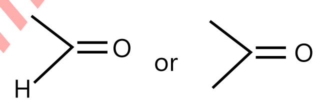
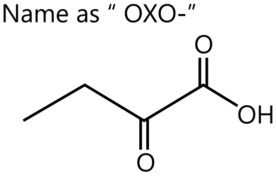
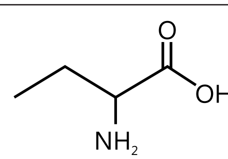


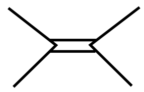
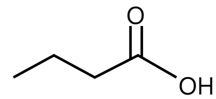
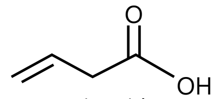
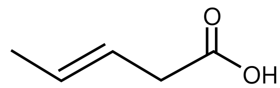
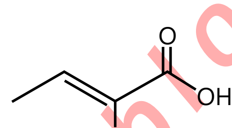
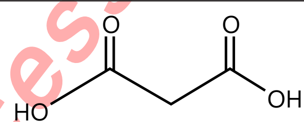
2-Methylpentanoic acid
(β-Methylvaleric acid)



3-Chloropropanoic acid
(γ-Chloropropionic acid)

Table 24.2: IUPAC naming of substituted carboxylic acid

(1) Naming carboxyl groups attached to a ring	- Carboxyl group added to a ring. - Suffix " carboxylic acid" added to name of the cyclic compound	Example  Cyclopentanecarboxylic acid  Cis-2-Bromocyclohexanecarboxylic acid
(2) Naming carboxylates	- Carboxyl group attached to a cation Sodium → Cation Acetate → "-ic acid" replaced by "-ate"	 Sodium ethanoate (Sodium Acetate)  Potassium Propanoate (Potassium propionate)
(3) Naming the acids containing other functional groups (-COOH = highest priority)	i) Hydroxyl substituent –OH 'ℓ' from hydroxyl is removed	 2, 4- Dihydroxybutanoic acid
	ii) Aldehyde / ketone substituent  Aldehyde / Ketone	Name as " OXO-"  2- Oxobutanoic acid
	iii) Amino substituent – NH_2	 2-Aminobutanoic acid

	iv) Alkene substituent  cis/trans or E/Z nomenclature for the alkene needs to be included if necessary.	 Butanoic acid  3-Butenoic acid ↓ Position  Trans-3-pentenoic acid  (E) -2-Methyl-2-butenoic acid
(4) Di-carboxylic acids	- Carboxyl groups occupy the ends of the chain	 Propanedioic acid

4.PHYSICAL PROPERTIES OF ACIDS AND ACID DERIVATIVES

(a) Physical appearance and odour

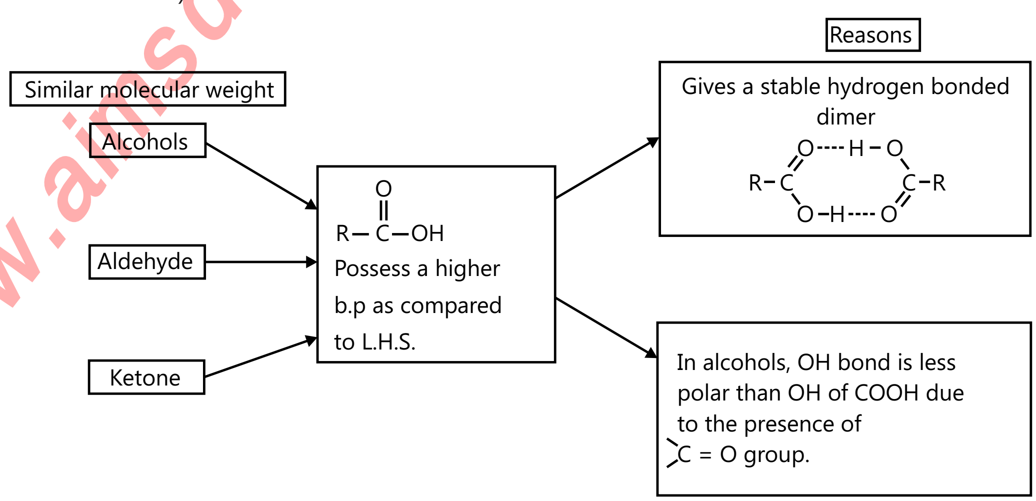
$C_1 - C_3$ = Liquid = Colourless & pungent smelling

$C_4 - C_6$ = Liquid (oily) = Colourless & unpleasant smell

C > C_7 = waxy solids= Colourless

(b) Boiling oints: Refer the following Flow-chart for a better understanding.

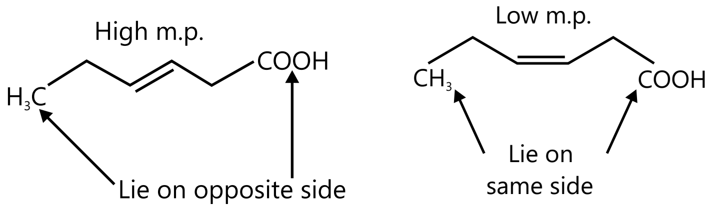
(L.H.S.=Left Hand Side)



Flowchart 24.3: Comparison of B.p of carboxylic acid with other carbonyl compound

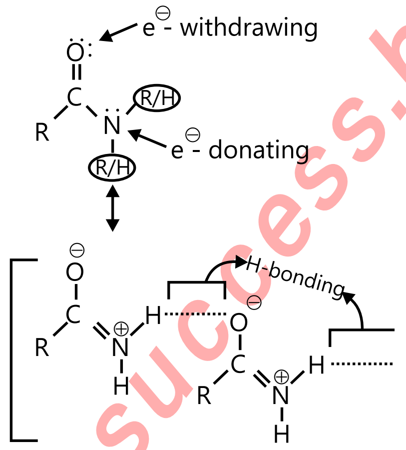
(c) Melting Points:

(i) Carboxylic acid with more than 8 carbon atom and a double bond have low melting point due to the inability to form a stable lattice.



(ii) Structures with even number of C atoms have a higher melting point as compared to structures having odd number of C-atoms.

(iii) The high M.Pof primary and secondary amides is due to the strong hydrogen bonding and the presence of electron-withdrawing and electron-donating group.



(d) Solubility:

(i) Lower carboxylic acid $(C_1 - C_2)$ are - miscible with water acids

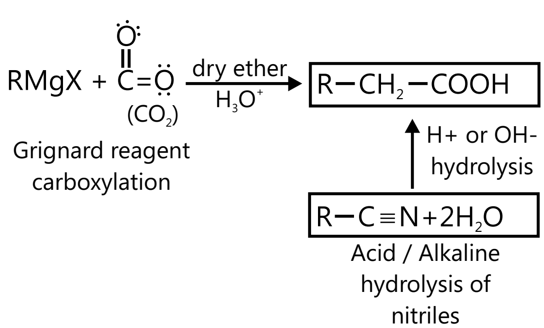
(ii) Instead of dimerization, they form H-bonds with water.

(iii) As the length of chain increases, the solubility decreases.

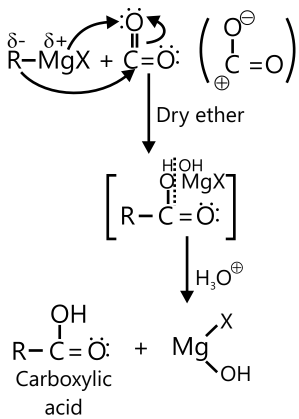
(iv) The derivatives like acid chlorides and anhydrides react with solvents like H_2O & alcohol.

5. METHODS OF PREPARATION OF CARBOXYLIC ACIDS

General reaction of preparation of carboxylic acid



(a) Synthesis of carboxylic acids by the carboxylation of Grignard reagents

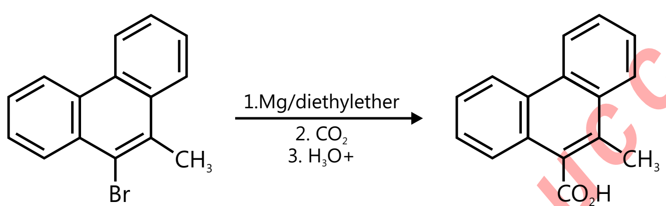


-RMgX acts as a nucleophile

Example:

$$CH_3\underset{\underset{Cl}{|}}{C}HCH_2CH_3 \xrightarrow[\text{2. } CO_2 \quad \text{3. } H_3O^+]{\text{1. Mg / diethyl ether}} CH_3\underset{\underset{CO_2H}{|}}{C}HCH_2CH_3$$

2-Chlorobutane — 2-Methylbutanoic acid (78 - 88%)



9-Bromo-10-methylphenanthrene — 10-Methylphenanthrene-8-carboxylic acid

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-MgBr \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } CO_2} CH_3-\underset{\underset{CH_3}{|}}{CH}-COOH$$

Isobutyric acid (2-methyl propanoic acid)

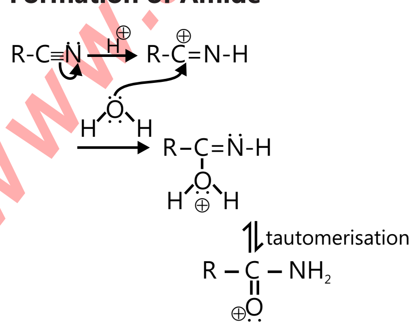
(b) Synthesis of Carboxylic acids by the hydrolysis of nitriles Mechanism:

Hydrolysis of cyanides (Acid catalysed):

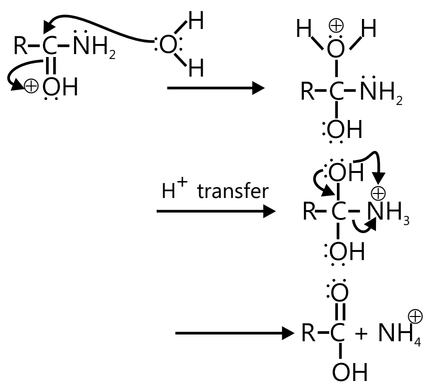
$$\underset{\text{Nitrile}}{RC\equiv N} + \underset{\text{Water}}{2H_2O} + H^+ \xrightarrow{\text{Heat}} \underset{\text{Carboxylic acid}}{R-\overset{\overset{O}{||}}{C}-OH} + \underset{\text{Ammonium ion}}{NH_4^+}$$

Mechanism:

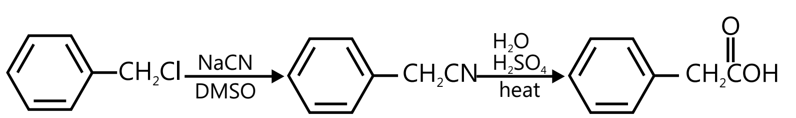
(a) Formation of Amide



(b) Formation of Acid



Example:



Benzyl chloride Benzyl cyanide (92%) Phenylacetic acid (77%)

PLANCESS CONCEPTS

- Alkyl cyanides needed for the purpose can easily be prepared from the corresponding alkyl halides with alcoholic KCN or NaCN.

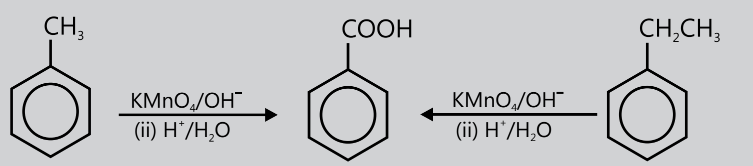
  $R - Cl + KCN \rightarrow R - C \equiv N + KCl$

- This reaction is used to ascend the series having one carbon atom more than the corresponding alkyl halides which are prepared from alcohol on treating with phosphorus halide.

  $ROH + PX_5 \rightarrow R - X + POX_3 + HX$

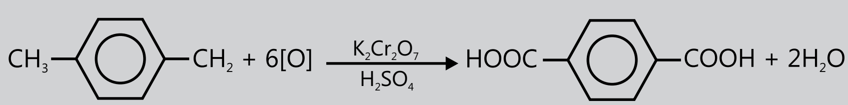
- This hydrolysis of alkyl cyanide provides a useful method to get carboxylic acid having one carbon atom more than the original alkyl halide and alcohols.

By Oxidation of alkyl benzenes – aromatic acids are produced.



Toluene Benzoic acid Ethylbenzene

E.g



p-Xylene Terephthalic acid

Vaibhav Krishnan (JEE 2009, AIR 22)

6. CHEMICAL REACTIONS

6.1. Acidic Strength

Acidity of carboxylic acids :

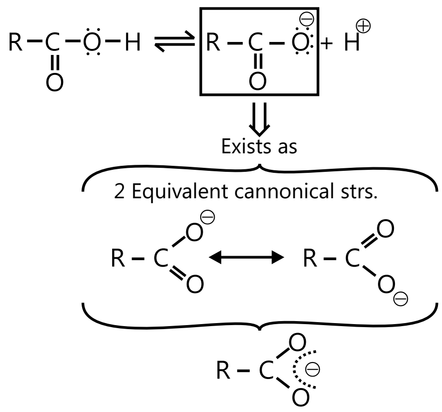
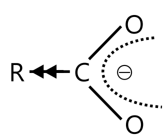
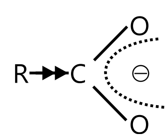


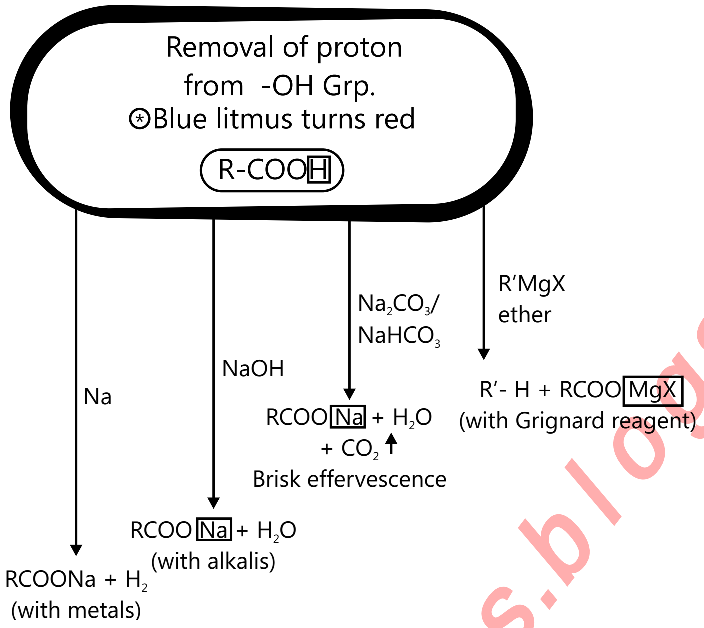
Table 24.3: Comparative acidity of Carboxylic acid with electron withdrawing group vs Carboxylic acid with electron donating group

R= Electron withdrawing Group	R= Electron Donating Group
⇒ Shows -I effect ⇒ Stabilises anion & increases acidic nature ⇒ Example 	⇒ Shows +I effect ⇒ Destabilizes anion & decrease acidic nature ⇒ Example 
∴ $F–CH_2COOH > Cl–CH_2COOH > Br–CH_2COOH$ OR ← Increasing acid strength —— $CCl_3–COOH > Cl–CHCl–COOH > Cl–CH_2COOH$	$HCOOH > CH_3COOH > CH_3–CH_2–COOH$ $(COOH)_2 > CH_2(COOH)_2 > (CH_2–COOH)_2$ $\boxed{\therefore RCOOH > HOH > ROH > HC\equiv CH > NH_3 > RH}$

Tips and Tricks

Acidity of acids is compared by comparing stability of conjugate base

6.2 Reactions Involving Removal of Proton From–OH Group



Flowchart 24.4: n Reaction involving displacement of H from -OH group.

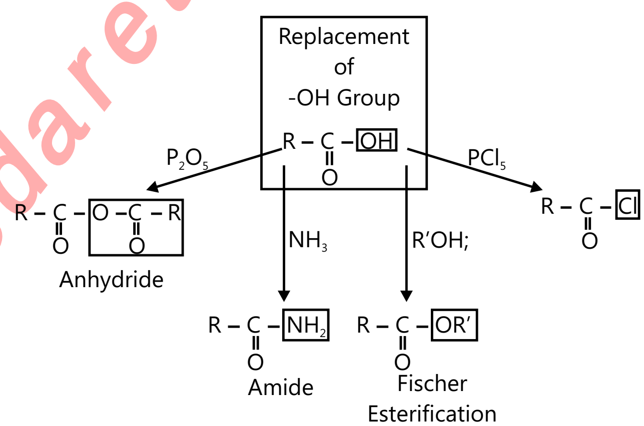
Important Point:

A stronger acid displaces a weaker acid from the salt of the weaker acid.

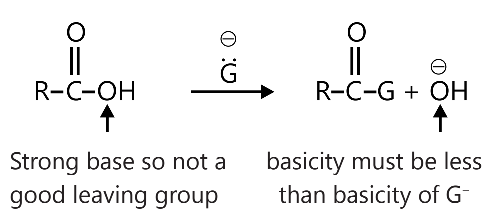
Example: CH_3COOH (Strongeracid) $+ CH_3ONa \rightarrow CH_3COONa + CH_3 - OH$

Example: CH_3COOH (Stronger acid) + $NaHCO_3 \rightarrow CH_3COONa + H_2CO_3$ (Weaker acid) $\rightarrow H_2O + CO_2\uparrow$ (lab. test of carboxylic acid)

6.3 Reactions Involving Replacement of –OH Group



Flowchart 24.5: Reaction Involving removal of OH group.



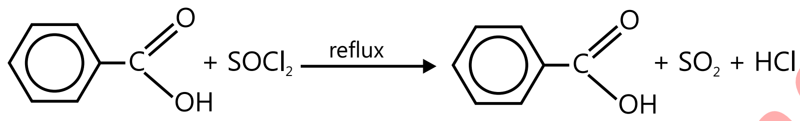
(a) Formation of acid chlorides

$$R\text{-}COOH \xrightarrow[\text{Pyridine}]{PCl_5} R\text{-}\overset{\overset{O}{\|}}{C}\text{-}Cl + POCl_3 + HCl$$

$$R\text{-}COOH \xrightarrow[\text{Pyridine}]{PCl_3} R\text{-}\overset{\overset{O}{\|}}{C}\text{-}Cl + H_3PO_3$$

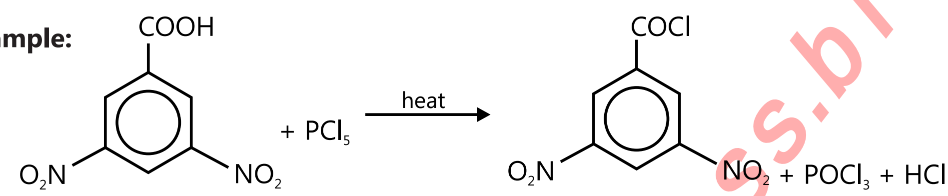
$$R\text{-}COOH \xrightarrow{SOCl_2} R\text{-}\overset{\overset{O}{\|}}{C}\text{-}Cl + SO_2 + HCl$$

Example:



Benzoic acid　　　Benzoyl chloride

Example:



3, 5-Dinitrobenzoic acid　　　3, 5-Dinitrobenzoyl chloride

(b) Fisher Esterification: Carboxylic acid react with alcohol to form esters through a condensation reaction known as esterification.

General Reaction:

$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH + R'\text{-}OH \underset{}{\overset{H^{\oplus}}{\rightleftharpoons}} R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OR' + H_2O$$

Specific Examples:

$$CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH + CH_3CH_2\text{-}OH \overset{H^{\oplus}}{\rightleftharpoons} CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}OC_2H_5 + H_2O$$

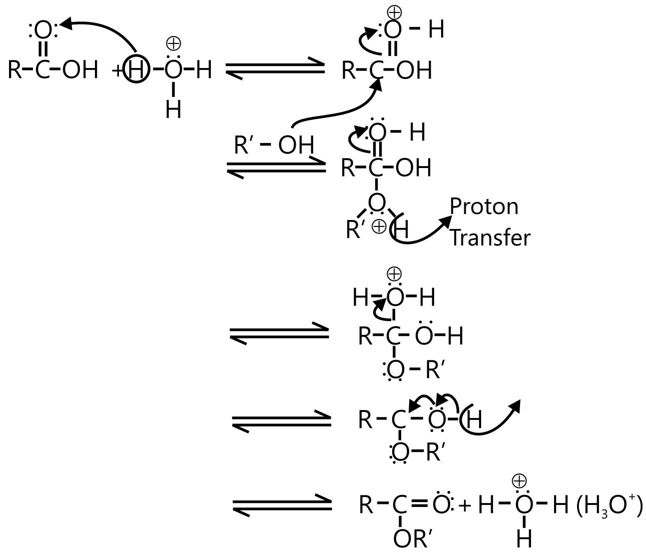
$$C_6H_5\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH + CH_3\text{-}OH \overset{H^{\oplus}}{\rightleftharpoons} C_6H_5\text{-}\overset{\overset{O}{\|}}{C}\text{-}OCH_3 + H_2O$$

Mechanism : (Acid catalysed esterification)

(i) A reactive electrophile is generated by addition of a proton or a Lewis acid.

(ii) A tetrahedral intermediate containing two equivalent hydroxyl groups is obtained by the nucleophilic attack of the alcohol .

(iii) Elimination of these hydroxyl groups after a proton shift (tautomerism) occurs leading to the formation of water and the ester.



The forward reactions give acid catalysed esterification of an acid while the reverse account for the acid catalysed hydrolysis of an ester

Acid catalysed ester hydrolysis.

$$R-\overset{O}{\overset{\|}{C}}-OR' + H_2O \xrightleftharpoons{H_3O^{\oplus}} R-\overset{O}{\overset{\|}{C}}-OH + R'-OH$$

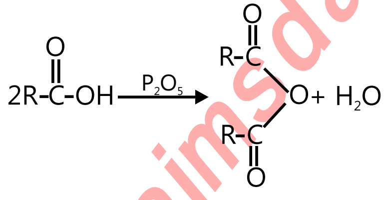
For esterification of an acid we can use an excess of the alcohol and removal of water to prevent the reverse reaction, Hydrolysis of an ester uses a large excess of water and refluxing the ester with dilute aqueous HCl or dilute aqueous H_2SO_4 occurs.

(c) Formation of amides:

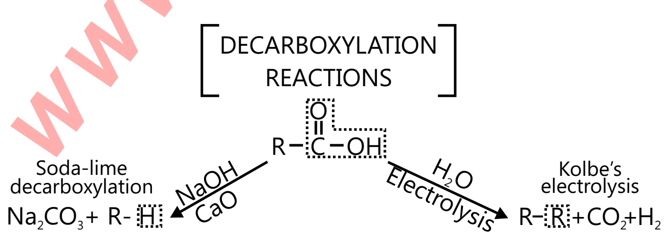
$$R-\overset{O}{\overset{\|}{C}}-OH + NH_3 \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\overset{\oplus}{N}H_4 \xrightarrow{150\text{-}200^\circ C} R-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$$

In fact, amides cannot be prepared from carboxylic acids and amines unless the ammonium salt is heated strongly to dehydrate it. This is not usually a good method of preparing amides.

(d) Formation of acid anhydride:

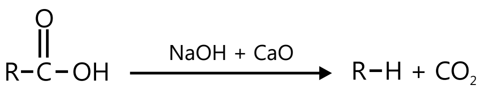


6.4 Decarboxylation Reactions

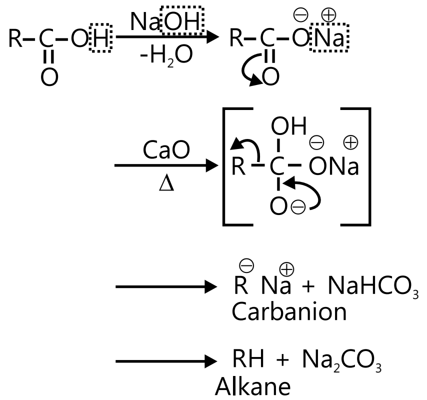


(a) Soda-lime decarboxylation:

General reaction:



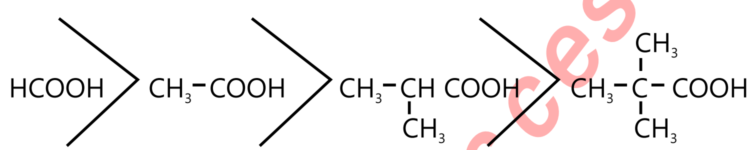
Mechanism



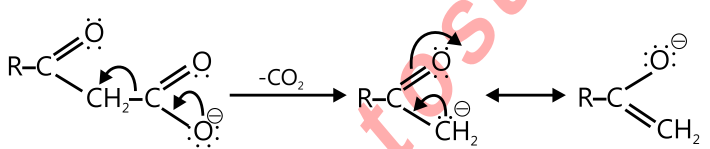
(i) The stability of carbanion intermediate decides the rate of reaction .

(ii) Rate of decarboxylation increases with the presence of electron withdrawing group at R-COOH.

Example:



(iii) Presence of some functional groups on aliphatic acids enable the decarboxylation.



Resonance
stabilized anion

Aliphatic acids that do undergo successful decarboxylation have certain functional groups or double or triple bonds in the α or β positions.

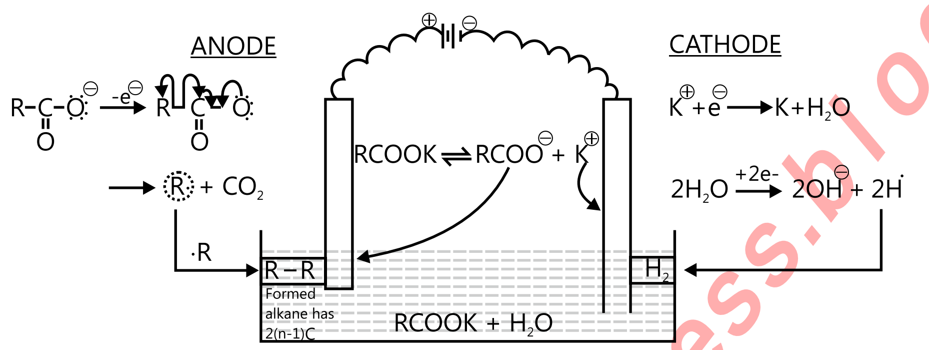
Table 24.4: Decarboxylation product of substituted carboxylic acid

		Acid type	Decarboxylation product
(1)	Malonic	HOOC – C – COOH	HOOC – C – H
(2)	α-Cyano	NC – C – COOH	NC – C – H
(3)	α-Nitro	O_2N – C – COOH	O_2N – C – H
(4)	α-Aryl	Ar – C – COOH	Ar – C – H

		Acid type	Decarboxylation product
(5)	β-Keto	$-\underset{\underset{O}{\parallel}}{C}-\overset{\vert}{\underset{\vert}{C}}-COOH$	$-\underset{\underset{O}{\parallel}}{C}-\overset{\vert}{\underset{\vert}{C}}-H$
(6)	α, α, α-Trihalo	$X_3C–COOH$	$X_3C–H$
(7)	β, γ-Unsaturated	$-\underset{\vert}{C}=\underset{\vert}{C}-\overset{\vert}{\underset{\vert}{C}}-COOH$	$-\underset{\vert}{C}=\underset{\vert}{C}-\overset{\vert}{\underset{\vert}{C}}-H$

(b) Kolbe's electrolysis

$$2RCOOK + 2HOH \xrightarrow{\text{Electrolysis}} R-R + 2CO_2 + H_2 + 2KOH$$



Example: $2CH_3-COOK + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3CH_3 + 2CO_2 + H_2 + 2KOH$

6.5 HVZ Reaction (Halogenation of Aliphatic Acids and Substituted Acids)

Converts a carboxylic acid possessing an α-hydrogen to an α-halocarboxylic acid when treated with phosphorus and halogen. It is called as Hell-Volhard-Zelinsky reaction where regioselectivity allows alpha-halogenation only.

$$CH_3COOH \xrightarrow{Cl_2,P} ClCH_2COOH \xrightarrow{Cl_2,P} Cl_2CHCOOH \xrightarrow{Cl_2,P} Cl_3CCOOH$$

Mechanism

(a) Carbonyl oxygen reacts with phosphorus trihalide to form a P-O bond giving the release of a halide anion.

(b) Attack of halide forms an intermediate to release a rearranged acyl halide, an acid and a phosphine oxide.

(c) Enol tautomer of acyl halide attacks the halogen molecule to form α-halo acyl halide.

(d) On hydrolysis, α-halocarboxylic acid is formed.

$$\underset{\text{An }\alpha\text{-halogenated acid}}{R\underset{\underset{Br}{\vert}}{C}HCOOH} + \text{large excess of } NH_3 \longrightarrow \underset{\text{An }\alpha\text{-amino acid}}{R\underset{\underset{NH_2}{\vert}}{C}HCOOH}$$

$$R\underset{\underset{Br}{\vert}}{C}HCOOH + NaOH \longrightarrow R\underset{\underset{OH}{\vert}}{C}HCOONa \xrightarrow{H^+} \underset{\text{An }\alpha\text{-hydroxy acid}}{R\underset{\underset{OH}{\vert}}{C}HCOOH}$$

$$RCH_2\underset{\underset{Br}{\vert}}{C}HCOOH + KOH\ (alc) \longrightarrow RCH=CHCOO^- \xrightarrow{H^+} \underset{\text{An }\alpha,\beta\text{-unsaturated acid}}{RCH=CHCOOH}$$

7. CARBOXYLIC ACID DERIVATIVES

Functional derivatives of carboxylic acids

-Acid chlorides

-Anhydrides

-Amides

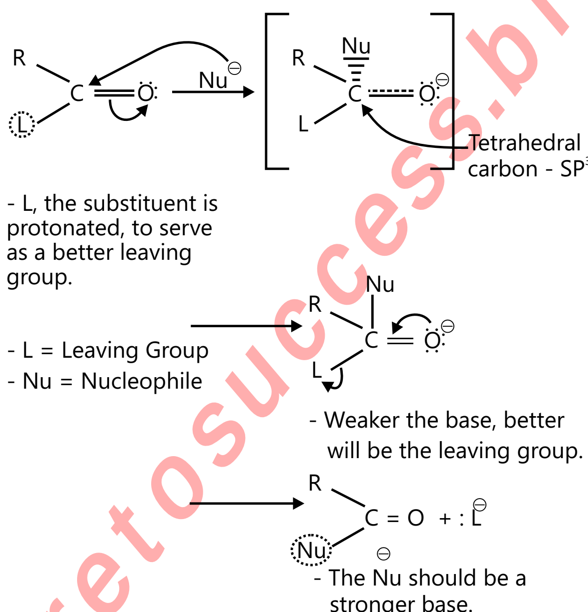
-Esters

The above are compounds in which the replacement of –OH of a carboxyl group is done by –Cl, –COOR , $-NH_2$, or –OR.

Characteristic reaction of acid derivatives (Nucleophilic acyl substitution):

Nucleophilic acyl substitution

-An addition - elimination mechanism

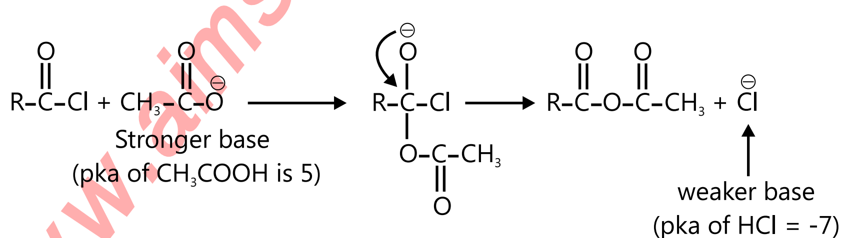


$$\boxed{L = -X > -O-\overset{O}{\overset{\|}{C}}-R > -OR > -OH > -NH_2}$$

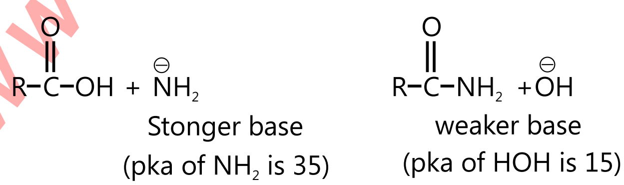
[Order of Reactivity]

Examples:

(a)



(b)



(c) $$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + \underset{pk_a\,=\,16}{ROH} \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OR + \underset{pk_a\,=\,5}{CH_3CO\overset{\ominus}{O}}$$

(d) $$C_6H_5-\overset{O}{\overset{\|}{C}}-OCH_3 + \underset{pk_a\,=\,35}{NH_3} \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-NH_2 + \underset{pk_a\,=\,16}{CH_3\overset{\ominus}{O}}$$

(e) $$C_6H_5-\overset{O}{\overset{\|}{C}}-NH_2 + \underset{pk_a\,=\,16}{CH_3OH} \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-OCH_3 + \underset{pk_a\,=\,35}{\overset{\ominus}{N}H_2}$$

PLANCESS CONCEPTS

Condition for nucleophilic substitution reaction:

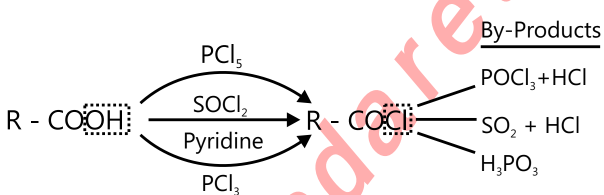
$$R-\overset{O}{\overset{\|}{C}}-L + \overset{\ominus}{Nu} \longrightarrow R-\overset{O}{\overset{\|}{C}}-Nu + \overset{\ominus}{L}$$

- L must be better leaving group than $Nu^{\ominus}$, i.e., basicity of Nu should be more than that of L.
- Must be a strong enough nucleophile to attack RCOL.
- Carbonyl carbon must be enough electrophilic to react with

Nikhil Khandelwal (JEE 2009, AIR 94)

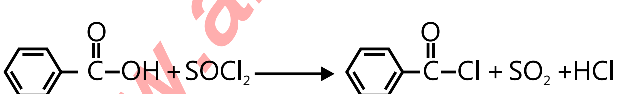
7.1 Acid Halides

(a) Methods of preparation Acyl halides



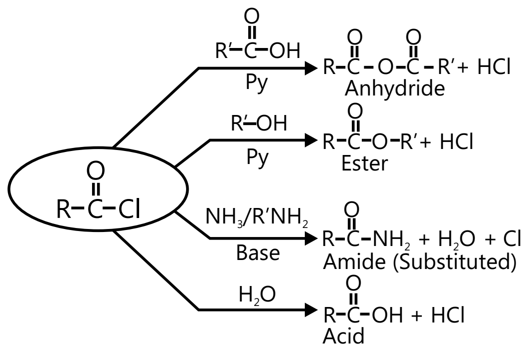
$$CH_3-\overset{O}{\overset{\|}{C}}-OH + SOCl_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-Cl + SO_2 + HCl$$

E.g Ethanoic acid Ethanoyl chloride



Benzoic acid Benzoyl chloride

(b) Chemical Reactions



Flowchart 24.5: General reactions of Acid halides

(i) Reaction with carboxylic acids

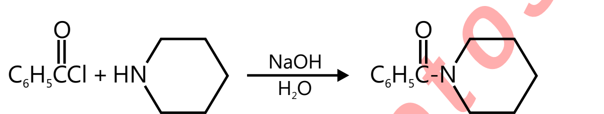
Carboxylic acids with acyl chlorides yield acid anhydrides with the help of a weak organic base, pyridine. Pyridine acts both as a catalyst and a base, which neutralizes the formed hydrogen chloride.

$$\underset{\text{Heptanoyl chloride}}{CH_3(CH_2)_5\overset{O}{\overset{\|}{C}}Cl} + \underset{\text{Heptanoic acid}}{CH_3(CH_2)_5\overset{O}{\overset{\|}{C}}OH} \xrightarrow{\text{Pyridine}} \underset{\text{Heptanoic anhydride (78 - 83\%)}}{CH_3(CH_2)_5\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}(CH_2)_5CH_3}$$

(ii) Reaction with alcohols

$$\underset{\text{Benzoyl chloride}}{C_6H_5\overset{O}{\overset{\|}{C}}Cl} + \underset{\text{tert-Butyl alcohol}}{(CH_3)_3COH} \xrightarrow{\text{Pyridine}} \underset{\text{tert-Butyl benzoate (80\%)}}{C_6H_5\overset{O}{\overset{\|}{C}}OC(CH_3)_3}$$

(iii) Reaction with ammonia and amines

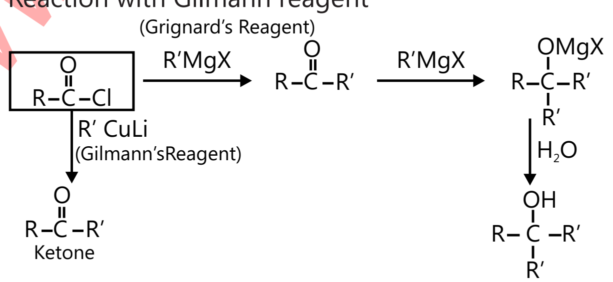


(iv) Hydrolysis

$$\underset{\text{Phenylacetyl chloride}}{C_6H_5CH_2\overset{O}{\overset{\|}{C}}Cl} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Phenylacetic acid}}{C_6H_5CH_2\overset{O}{\overset{\|}{C}}OH} + \underset{\text{Hydrogen chloride}}{HCl}$$

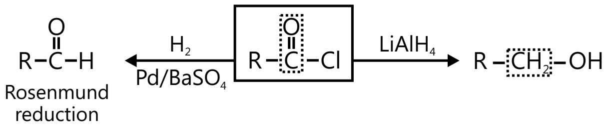
(v) Reaction of acid halide with organometallic

- With Grignard reagent
- Reaction with Gilmann reagent



(vi) Reduction of acid halides

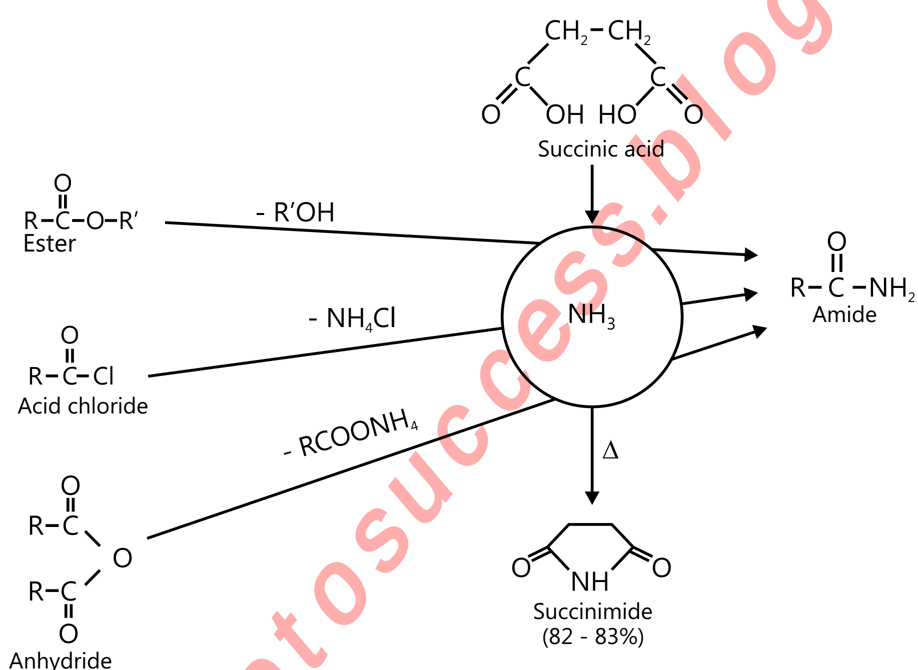
- By $LiAlH_4$
- By $H_2/Pd/BaSO_4$ (Rosenmund reduction)



7.2 Acid Amides

Methods of preparation of acid amide

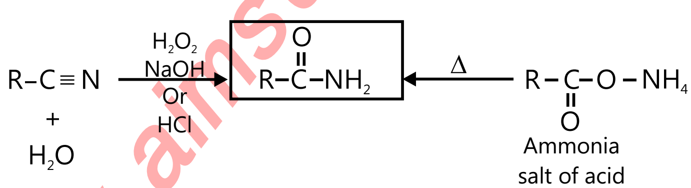
(a) With ammonia



Flowchart 24.6: Preparation of amides from acid derivative

(b) With (i) Cyanide (ii) Ammonia salt of acid

General reaction:



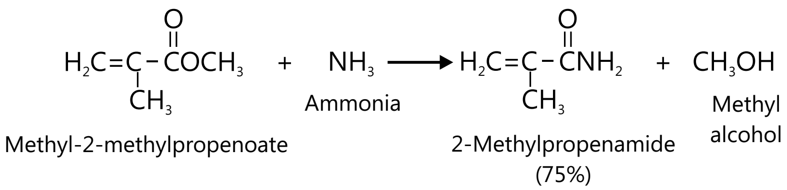
(i) From ammonia salts of carboxylic acid

$$CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2$$

(ii) From cyanides

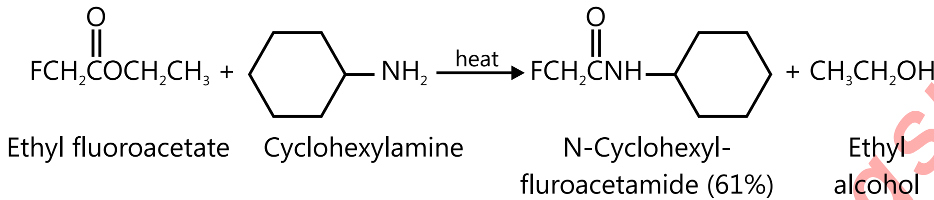
$$CH_3C \equiv N + H_2O \xrightarrow{dil.H_2SO_4} CH_3 - CONH_2$$

Example:



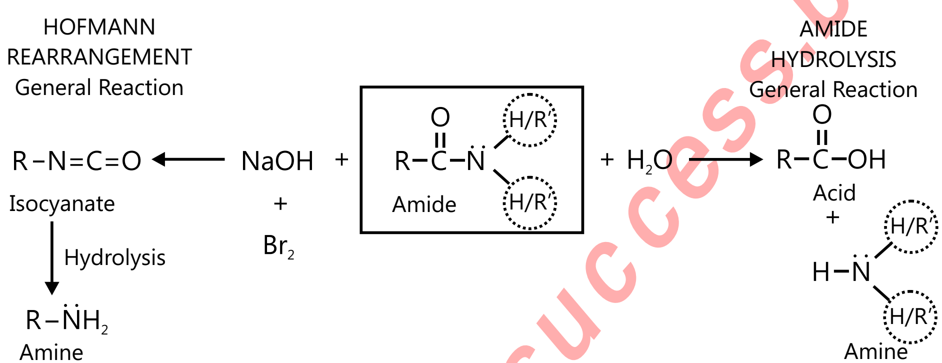
Amines, which are substituted derivatives of ammonia, react similarly

Example:



Important Chemical Reactions

General reaction:



(a) **Hoffmann rearrangement:** In the Hofmann rearrangement an unsubstituted amide is treated with sodium hydroxide and bromine to give a primary amine that has one carbon fewer than starting amide

General reaction:

$$R\text{–}\overset{\overset{\large O}{\|}}{C}\text{–}NH_2 + NaOH + Br_2 \longrightarrow \underset{\text{isocyanate}}{R\text{–}N{=}C{=}O} \xrightarrow{\text{Hydrolysis}} R\text{–}NH_2$$

Mechanism:

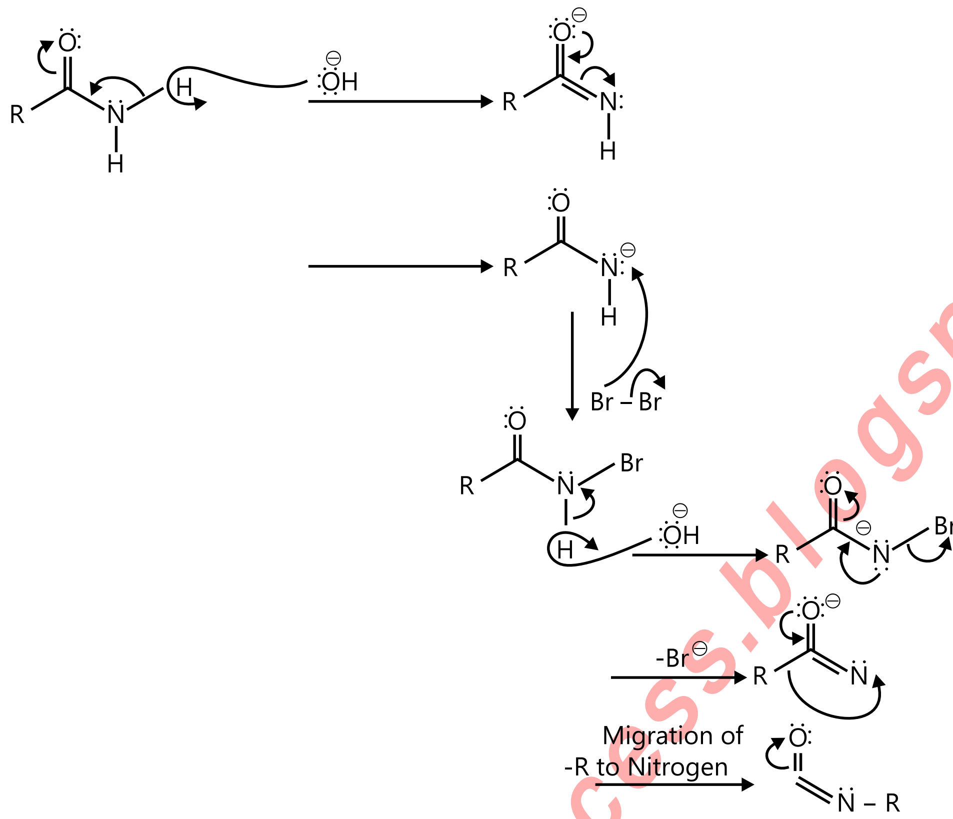
The mechanism is divided into 3 parts:-

(i) Formation of Isocyanate intermediate

(ii) Formation of carbamic acid

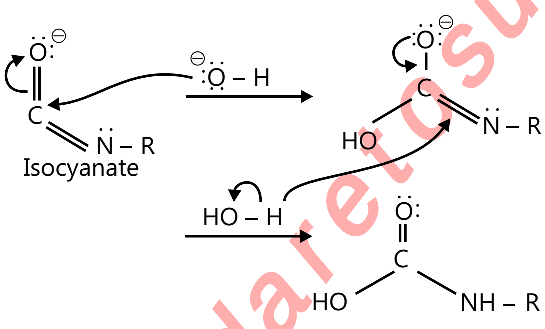
(iii) Decarboxylation to give Amine

(i) Formation of Isocyanate intermediate



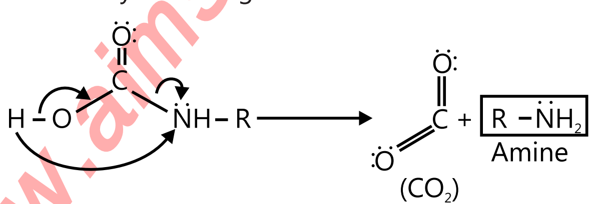
Isocyanate

(ii) Formation of carbamic acid

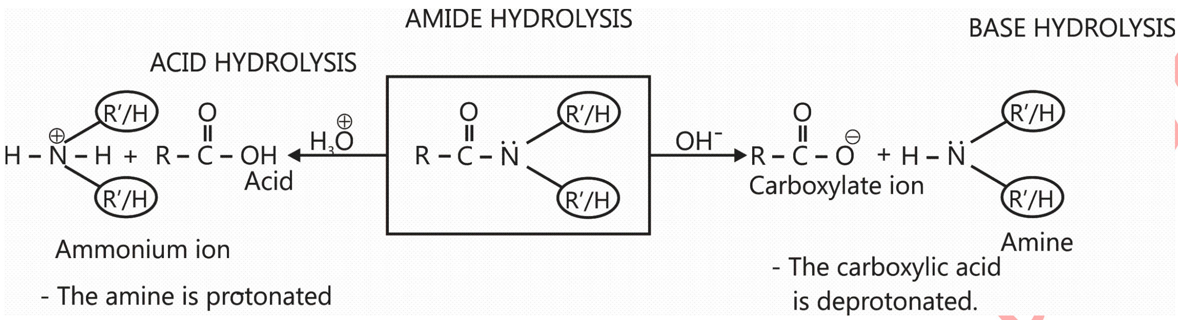


Carbamic acid

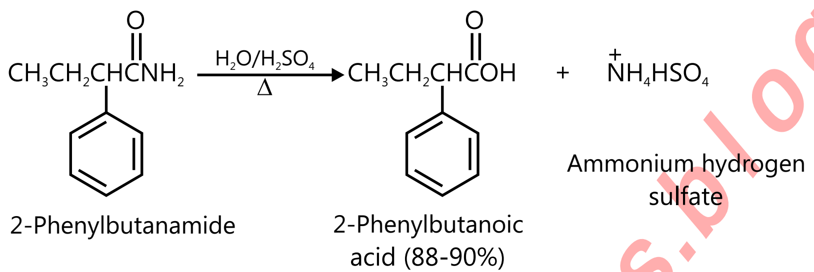
(iii) Decarboxylation to give Amine



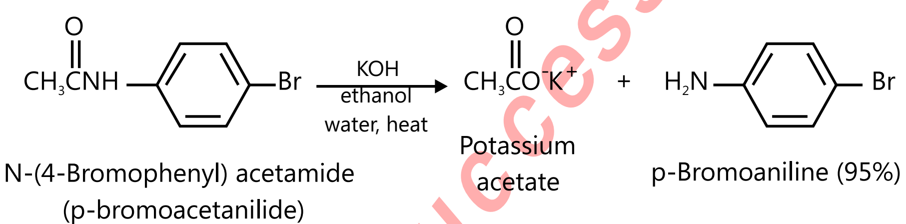
(b) Hydrolysis of amides



Example:

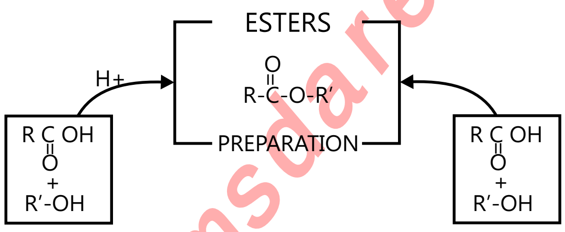


Example:



7.3 Esters

(a) Methods of Preparation



Examples:

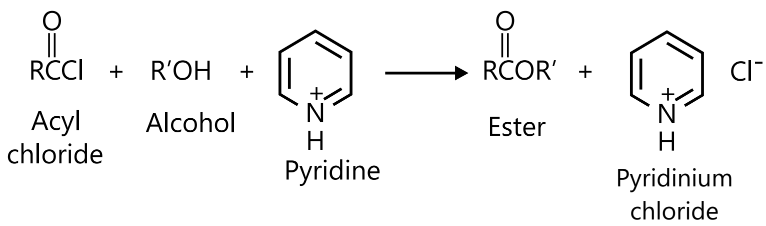
(i) $\underset{\text{Acetic acid}}{CH_3COOH} + C_2H_5OH \xrightarrow{H^+} CH_3COOC_2H_5 + H_2O$

$C_6H_5COOH + CH_3OH \xrightarrow{H^+} C_6H_5COOCH_3 + H_2O$

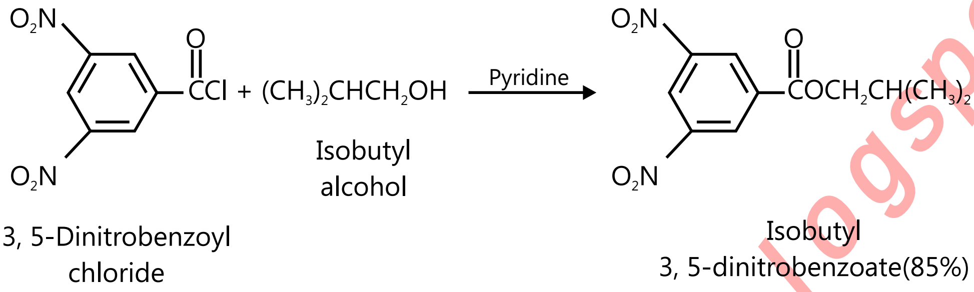
(ii) $CH_3COCl + C_2H_5OH \xrightarrow{\text{Pyridine}} CH_3COOC_2H_5 + HCl$

Alcohols react with acyl chlorides by nucleophilic acyl substitution to yield esters. These reactions are typically performed in the presence of a weak base such as pyridine.

Here conc. H_2SO_4 is used in the obove reactions which acts as a catalyst & a dehydeating agent.

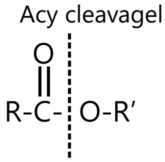


Example:



Example: $C_6H_5COCl + CH_3CH_2OH \xrightarrow{NaOH} C_6H_5COOCH_2CH_3 + HCl$

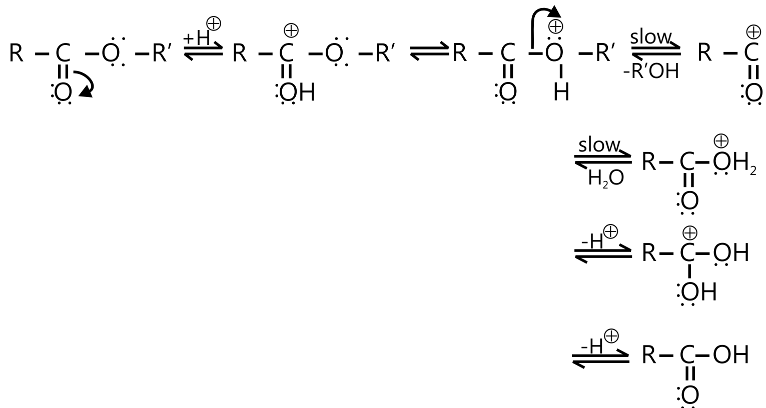
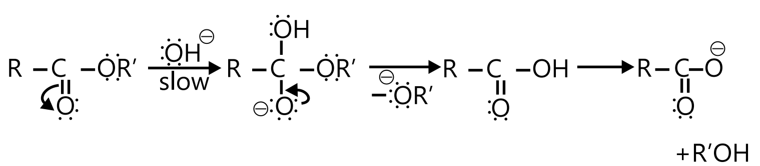
(b) Chemical Reactions: The acid and base catalysed ester hydrolysis involves the acyl cleavage of the ester group.



AAc_2 is Acid catalysed ester hydrolysis by acyl cleavage through bimolecular mechanism.

BAc_2 is Base catalysed ester hydrolysis by acyl cleavage through bimolecular mechanism.

Table 24.5: Mechanism of Acid catalysed and Base catalysed ester hydrolysis

Acid Catalysis	Acyl Cleavage	AAc_2	
Base Catalysis	Acyl Cleavage	BAc_2	

(i) Acid catalysed hydrolysis of ester (AAc_2):

$$CH_3-\overset{\overset{\large O}{\|}}{C}-O-R + H_2O \xrightleftharpoons{H^{\oplus}} CH_3COOH + ROH$$

The yield of products would be raised by adding excess of water.

$$CH_3-\overset{\overset{\large O}{\|}}{C}-OR + H_2O\ (\text{excess}) \xrightleftharpoons{H^{\oplus}} CH_3COOH + ROH$$

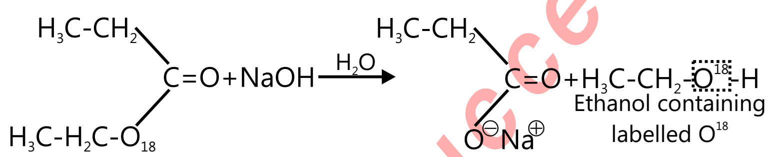
(ii) Base-Promoted Hydrolysis of Esters : Saponification (BAc_2):

The base catalysed hydrolysis is also known as Saponification.

$$\underset{\text{Ester}}{R\overset{\overset{\large O}{\|}}{C}-OR'} + NaOH \xrightarrow{H_2O} \underset{\text{Sodium carboxylate}}{R\overset{\overset{\large O}{\|}}{C}-O^-Na^+} + \underset{\text{Alcohol}}{R'OH}$$

The unreactive negatively charged carboxylate ion does not undergo nucleophilic substitution. The irreversible nature of this reaction,i.e., the base-promoted hydrolysis of an ester is seen over here. The mechanism for this reaction also involves a nucleophilic addition-elimination at the acyl carbon.

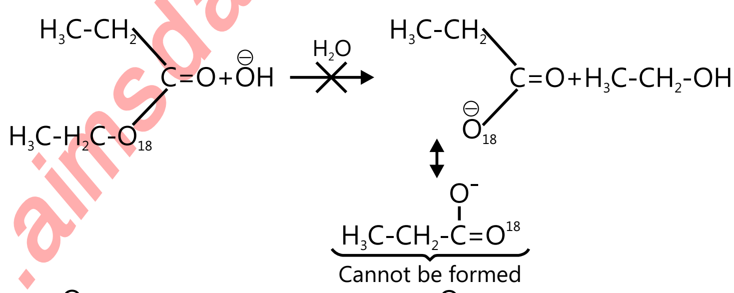
Mechanism:

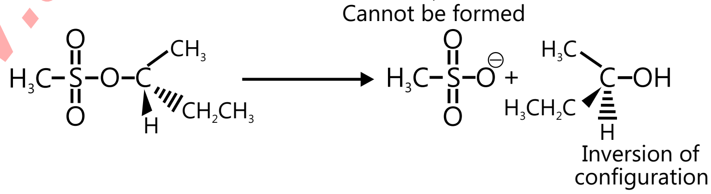


The mechanism is studied with the help of isotopically labelled esters. Ethyl propionate consisting of labelled ^{18}O in the ether-type oxygen of the ester undergoes hydrolysis with aqueous NaOH wherein the ^{18}O is observed to be contained in the produced ethanol only.

The result would have been different if it was an alkyl cleavage instead of the acyl one. But attack at the alkyl is not possible.

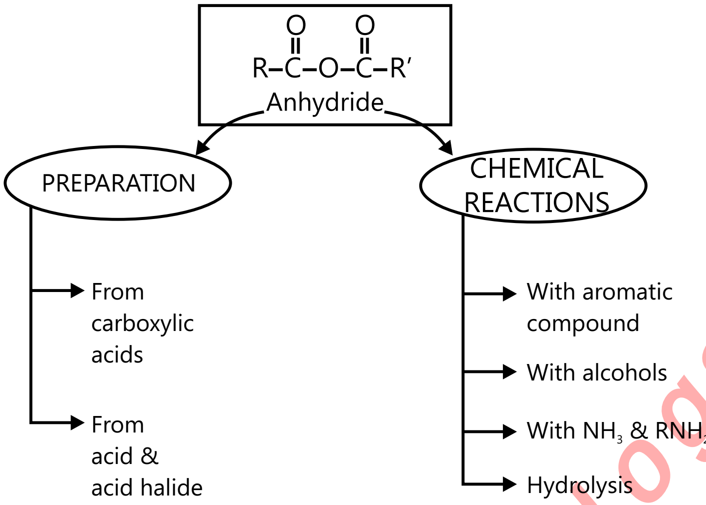
Such kind of attack of the nucleophile at the alkyl carbon occurs rarely in the case of carboxylic acid esters, but such attacks are preferred in case of esters of sulfonic acids (e.g. tosylates and mesylates)





Alkyl attack is seen in cases of alkyl sulfonates.

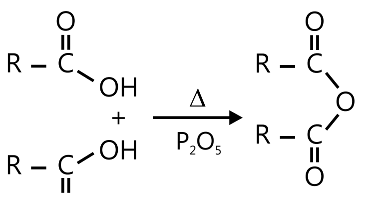
7.4 Acid anhydrides



Flowchart 24.6: Preparation and reactions of anhydride

(a) Method of Preparation

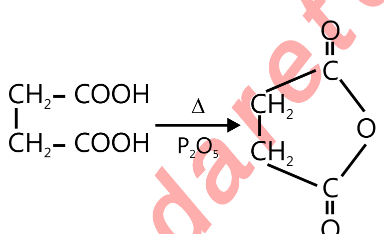
(i) From carboxylic acids



ANHYDRIDE

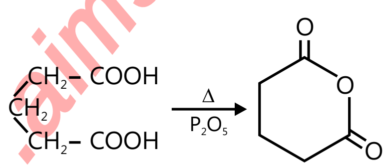
Example:

(i)

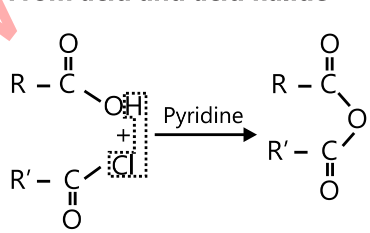


Succinic anhydride

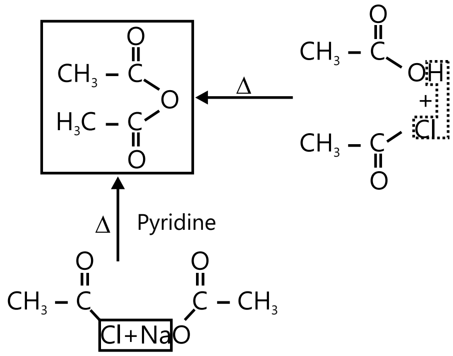
(ii)



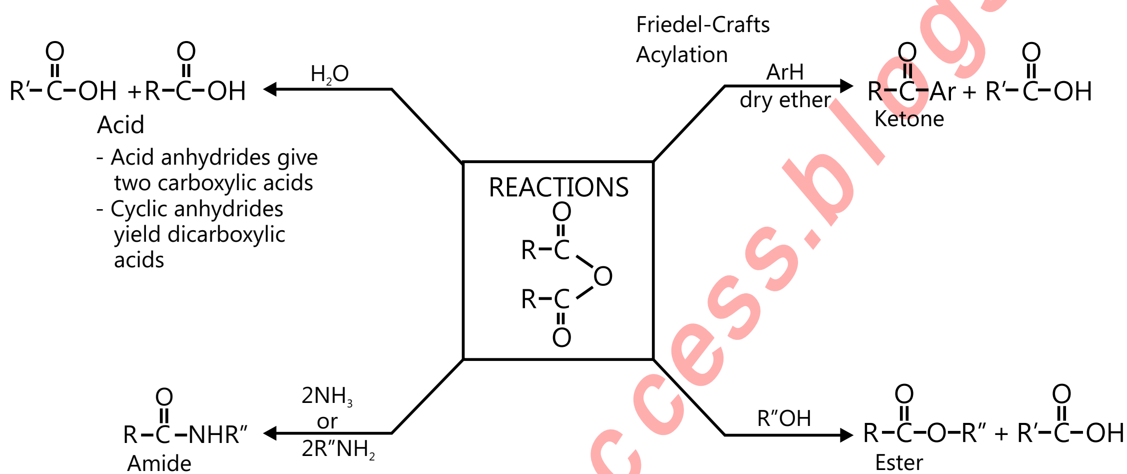
(ii) From acid and acid halide



Example:



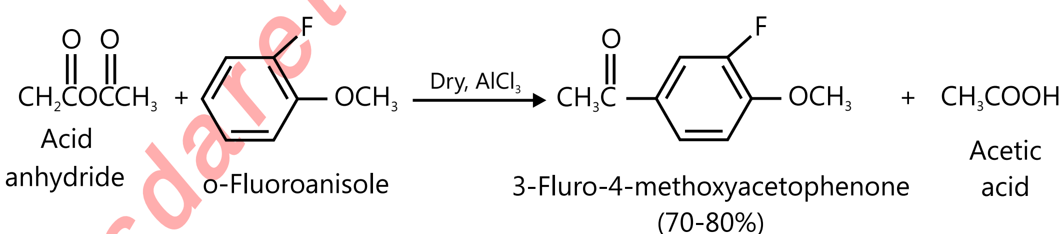
(b) Chemical Reaction



Flowchart 24.7: Important reaction of anhydride

(i) Reaction with aromatic compounds (Friedel-Crafts acylation)

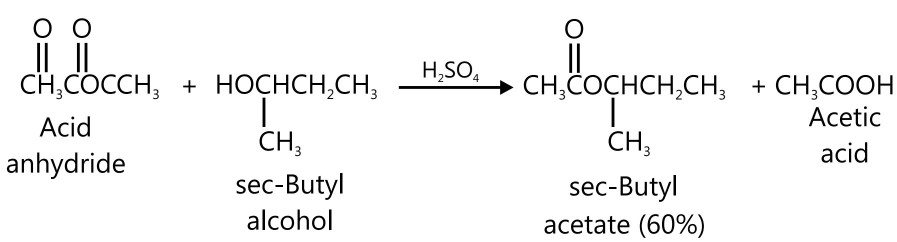
Example:



(ii) Reaction with alcohols: Esters are formed when acid anhydrides react with alcohols in presence of pyridine or a catalytic acid.

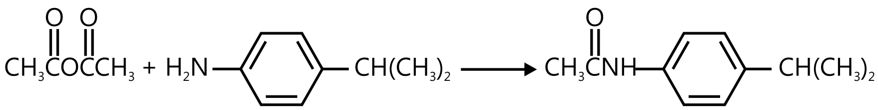
The below given example shows the incorporation of only one acyl group in the ester while the other forms an acetic acid molecule.

Example:



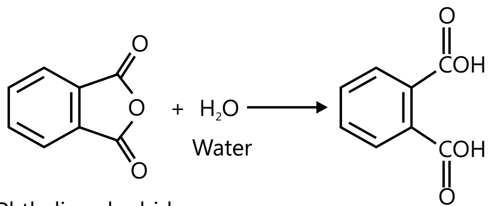
(iii) Reaction with ammonia and amines: Amides are formed when acid anhydride reacts with 2 molar equivalents of ammonia or amines.

The below given example shows the incorporation of only one acyl group into the amide and the other forms the amine salt of acetic acid.



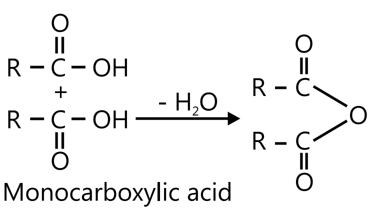
Acetic anhydride   p-Isopropylaniline   p-Isopropylacetanilide (98%)

(iv) Hydrolysis: Carboxylic acids are formed when acid anhydrides react with water. Cyclic anhydrides hydrolyse to dicarboxylic acids.



Phthalic anhydride   Water   Phthalic acid

8. HEATING EFFECTS



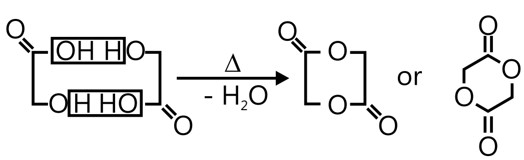
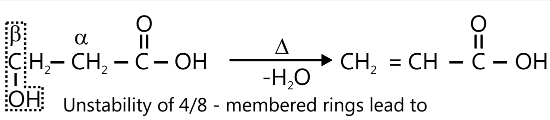
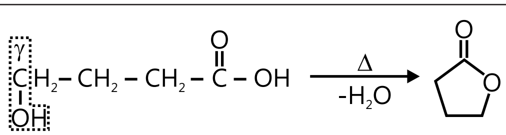
Anhydride

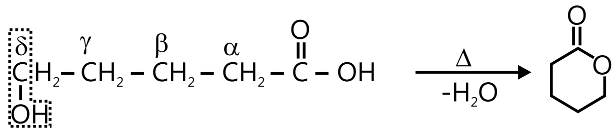
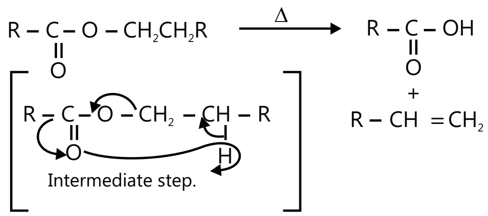
Monocarboxylic acid

$$CH_2(COOH)_2 \xrightarrow{-CO_2} CH_3-COOH$$ Acetic acid

Dicarboxylic acid

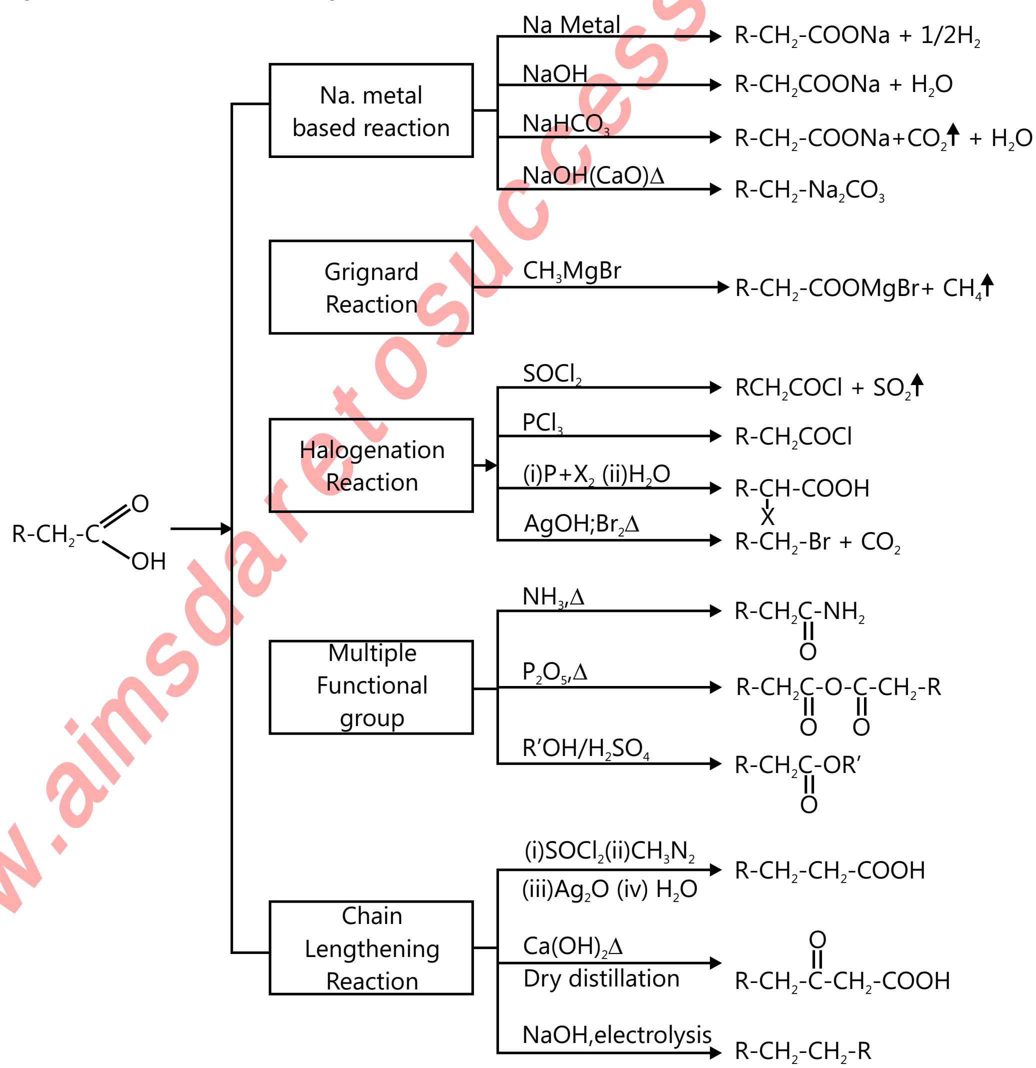
Table 24.8: Heating effects on hydroxy acids & ester

(1) α - Hydroxy acid	
(2) β - Hydroxy acid	 Unstability of 4/8 - membered rings lead to the formation of a,b - unsaturated acids
(3) γ - Hydroxy acid	

(4) δ - Hydroxy acid	
(5) Ester	

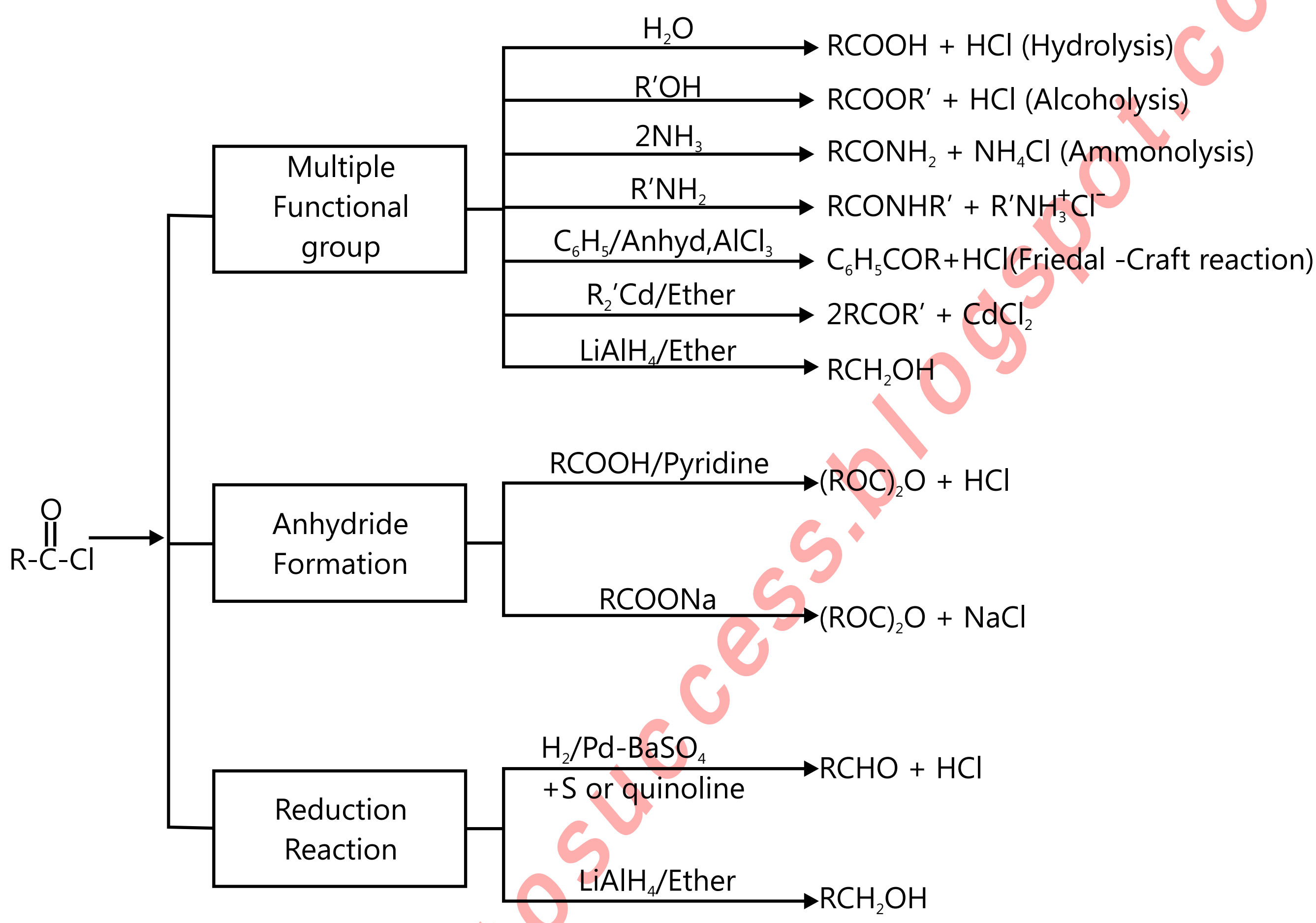
POINTS TO REMEMBER

(a) Summary of Reactions of Carboxylic Acids



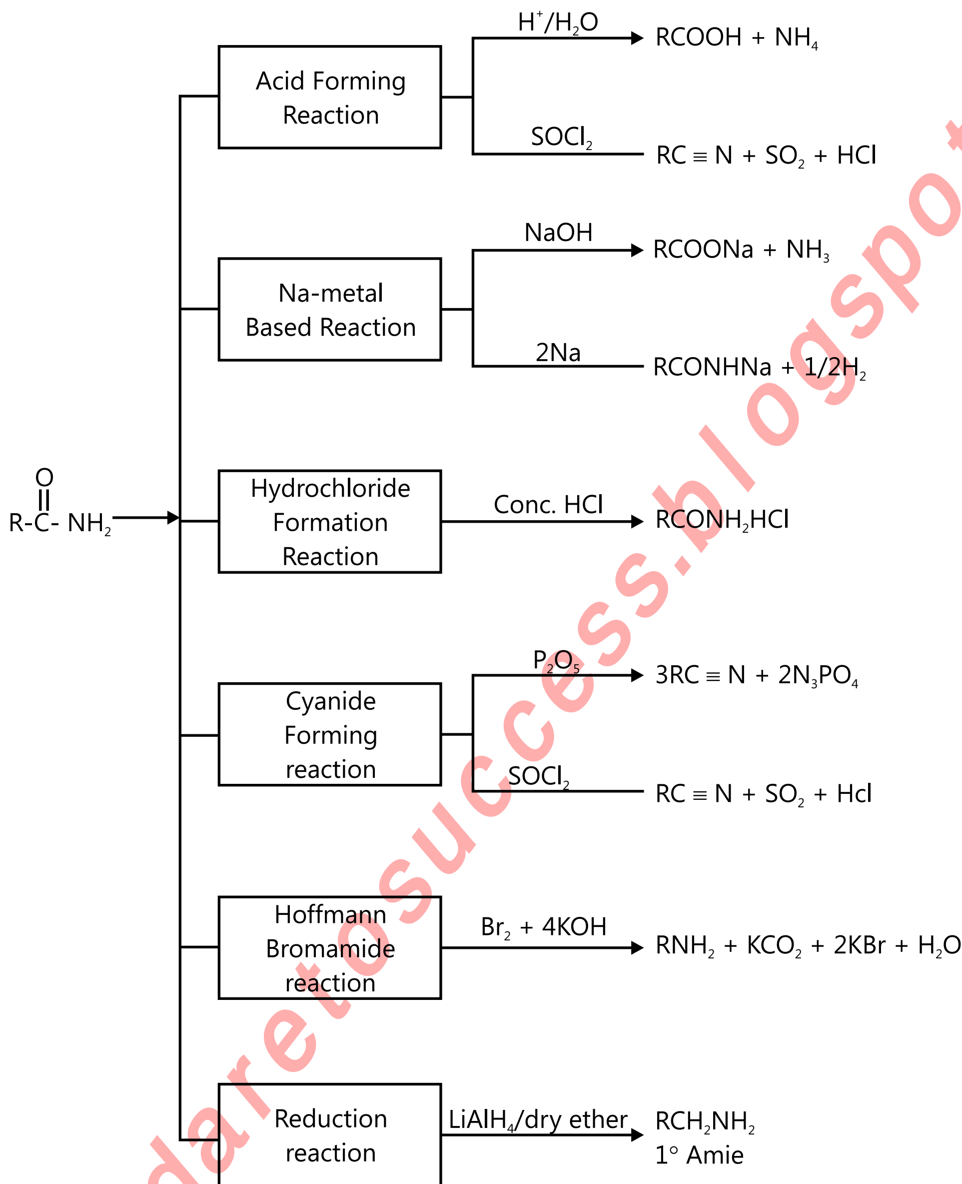
(b) Summary of Reactions of Acid Halides

Reaction of Acid Chloride



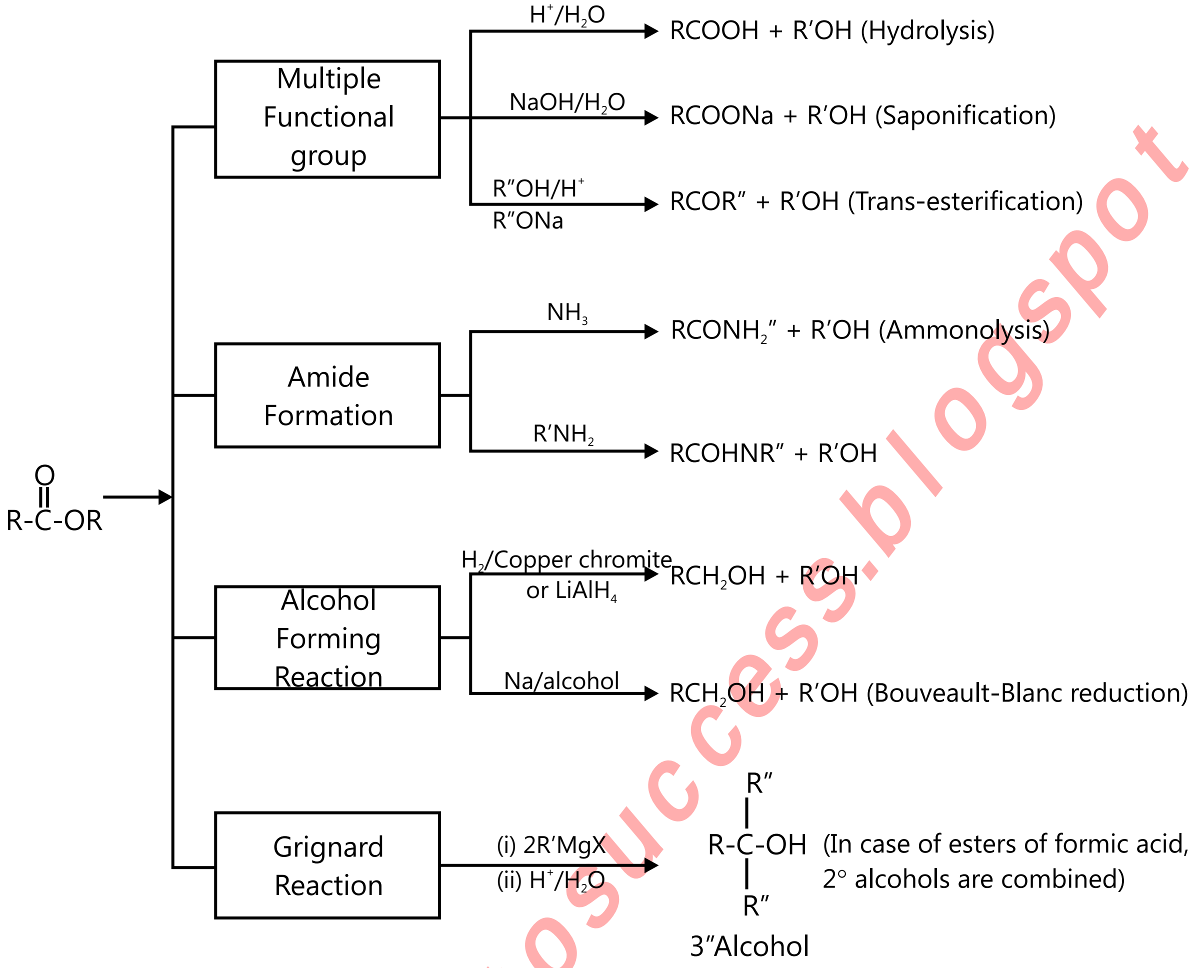
(c) Summary of Reactions of Amides

Reaction of amide



(d) Summary of Reactions of Esters

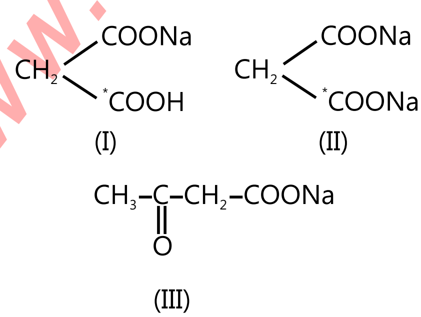
Reaction of Esters



Solved Examples

JEE Main/Boards

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



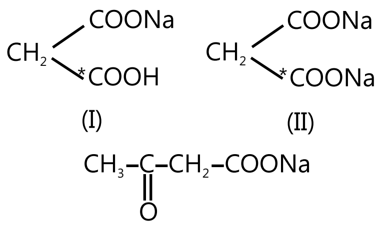
(A) (I) decarboxylates faster than (II) on heating.

(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.



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

Sol 2: (A, B, C, D) $H-\underset{\underset{O}{\|}}{C}-O \xrightarrow{Conc.NaOD} DCOO^- + DCH_2OD$

Cannizzaro reaction

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

Aldol + Cannizzaro reaction

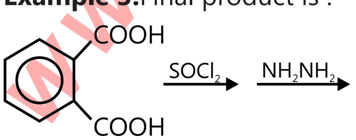
(C) $CH_3-CH_3-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{P+Br_2} CH_3-\underset{\underset{Br}{|}}{CH}-COOH$

HVZ reaction

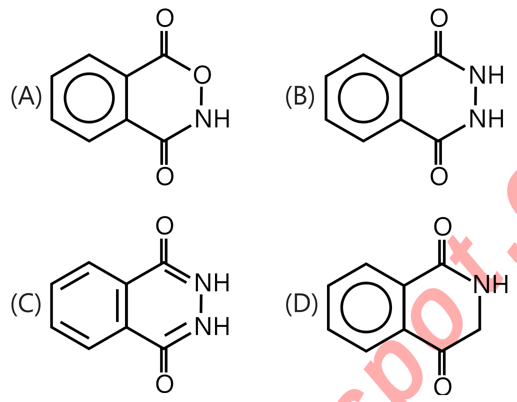
(D) $CH_3-\overset{\overset{H}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-\overset{18}{O}H + CH_3-CH_2-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{Conc.H_2SO_4} CH_3-CH_2-\underset{\underset{O}{\|}}{C}-\overset{18}{O}-\overset{\overset{H}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-CH_3$

(Esterification reaction)

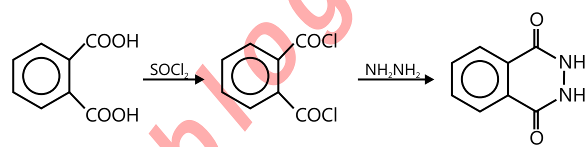
Example 3: Final product is :



Phthalic acid



Sol 3: (B)

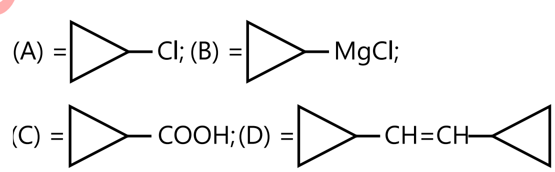


Example 4: Identify (A), (B), (C) and (D).

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

Sol: First step is preparation of gringnard reagent

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



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

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

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

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

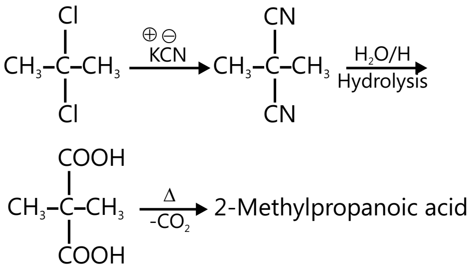
Example 6: Identify (A), (B) and (C).

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

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.



JEE Advanced/Boards

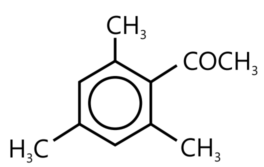
Example 1: Predict A, B, C, D and E.

$$\text{Acid(A)} \xrightarrow{\Delta} B \xrightarrow{\text{Mesitylene}/AlCl_3} C + CH_3COOH$$
$$C \xrightarrow{\text{Zn-Hg/Conc. HCl}} (D)$$

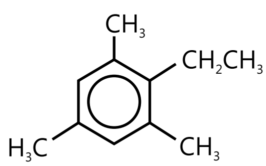
Sol 1: (A) = CH_3COOH;

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

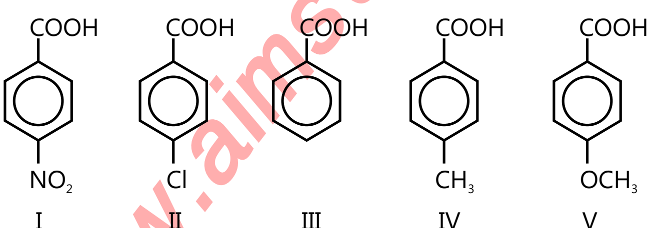
(c) =



(D) =



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



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) $CH_3-\underset{|\atop Br}{C}H-COOH$ (B) $CH_3-\underset{|\atop CN}{C}H-COOH$

(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.

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

Example 5: Which are correct against property mentioned?

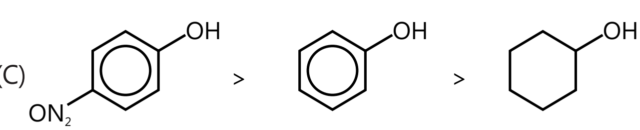
(A) $CH_3COCl > (CH_3CO)_2O > CH_3COOEt > CH_3CONH_2$

(Rate of hydrolysis)

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

(Rate of esterification)

(C)



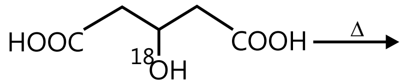
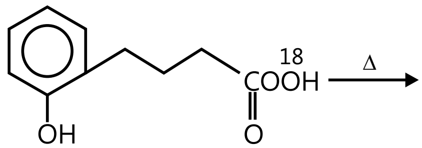
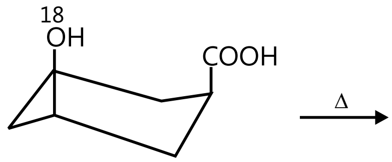
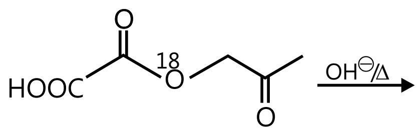
(Rate of esterification)

(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

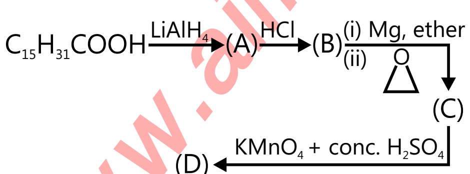
JEE Main/Boards

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?

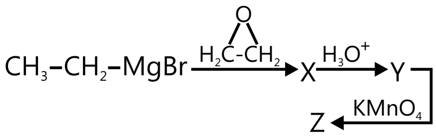
Q.7 Highly branched carboxylic acids are less acidic than unbranched acids. Why?

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 ?

$$HC\equiv CH \xrightarrow[\text{(ii) } 2CH_3I]{\text{(i) } 2NaNH_2} (X) \xrightarrow[H_2SO_4]{HgSO_4} (Y) \xrightarrow[\text{(ii)} H_3O^-]{\text{(i)} NaOH/Br_2} (Z)$$

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) $CH\equiv C–COOH$; (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.

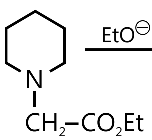
Q.28 An acidic compound (A), C_4H_8O loses its optical activity on strong heating yielding (B). $C_4H_6O_2$ which reacts readily with $KMnO_4$. (B) forms a derivative (C) with $SOCl_2$, which on reaction with $(CH_3)_2NH$ gives (D). The compound (A) on oxidation with dilute chromic acid gives an unstable 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.

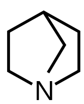
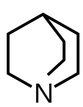
Q.30 An liquid (X) having molecular formula $C_6H_{12}O_2$ is hydrolysed with water in presence of an acid to give a carboxylic acid (Y) and an alcohol (Z). Oxidation of (Z) with chromic acid gives (Y). What are (X), (Y) and (Z) ?

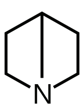
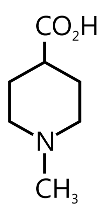
Exercise 2

Single Correct Choice Type

Q.1  $\xrightarrow{EtO^{\ominus}}$ $\xrightarrow[\Delta]{H_3O^{\oplus}}$ $\xrightarrow[HCl]{Zn(Hg)}$ (X)

Product (X) of above reaction is :

(A)  (B) 

(C)  (D) 

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

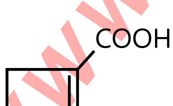
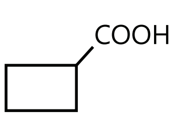
(I) MeCOCl (II) $MeCON_3$

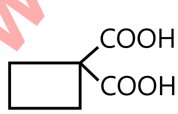
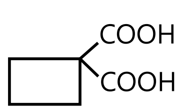
(III) MeCOOCOMe

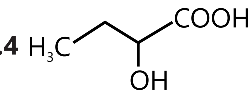
(A) I > II > III (B) II > I > III

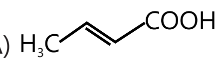
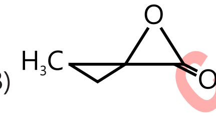
(C) I > III > II (D) II > III > I

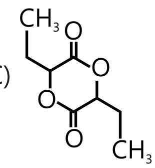
Q.3 $CH_2(COOEt)_2 + (CH_2)_3 \xrightarrow[EtOH]{NaOEt} I \xrightarrow{H_3O^+} II$ is :

(A)  (B) 

(C)  (D) 

Q.4  $\xrightarrow{\Delta}$ X, X will be

(A)  (B) 

(C)  (D) None

Q.5 $Me_3C-\overset{O}{\overset{\|}{C}}-\overset{18}{O}-CMe_3 \xrightarrow{dil.H_2SO_4}$ Product

of this reaction and the mechanism is :

(A) $Me_3C-\overset{O}{\overset{\|}{C}}-OH+Me_3C-\overset{18}{O}H$, $A_{AC}1$

(B) $Me_3C-\overset{O^{18}}{\overset{\|}{C}}-OH+Me_3C-OH$, $A_{AL}1$

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

(D) $Me_3C-\overset{O}{\overset{\|}{C}}-\overset{18}{O}H+Me_3C-OH$, $A_{AL}2$

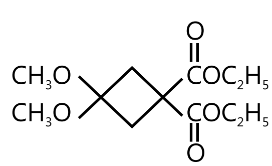
Q.6 Guess the product

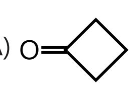
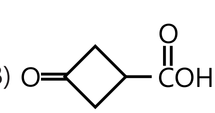
$CH_3CH_2CONH_2 \xrightarrow[\Delta]{PCl_5}$?

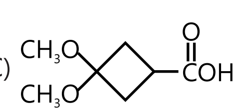
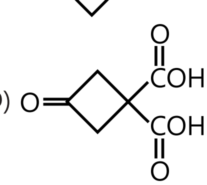
(A) CH_3CH_2-CN (B) CH_3CH_2COCl

(C) $CH_3CCl_2CONH_2$ (D) $CH_3CH_2CONHCl$

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



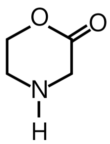
(A)  (B) 

(C)  (D) 

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

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

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

(C) 

(D) $MeCOONa + HOCH_2CH_2NH_2$

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

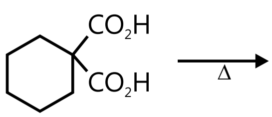
(A) $CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3$

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

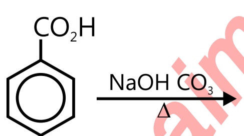
(C) $CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$

(D) All

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

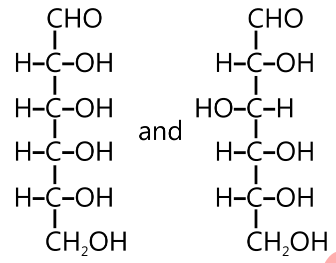
(A) 

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

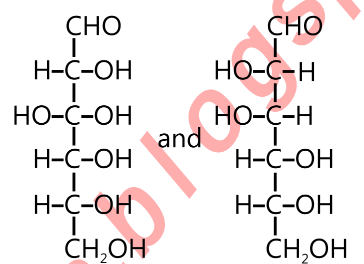
(C) 

(D) All

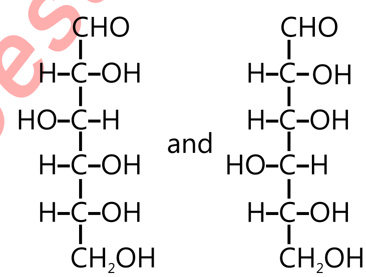
Q.11 Which of the following pair will form same osazone when it reacts phenyl hydrazine

(A) 

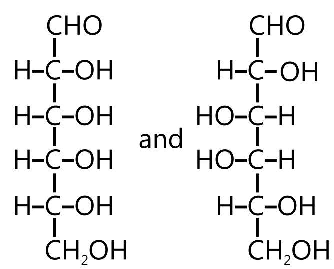
D-allose D-glucose

(B) 

D-glucose D-mannose

(C) 

D-glucose D-gulose

(D) 

D-allose D-glucose

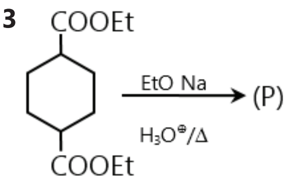
Q.12

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

Major product (X) is :

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

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

Q.13 

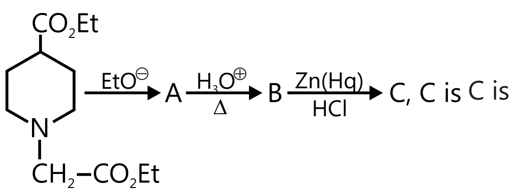
Select **incorrect** statement

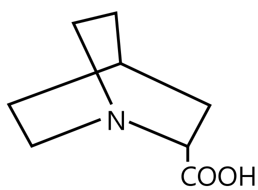
(A) P can turn blue litmus red

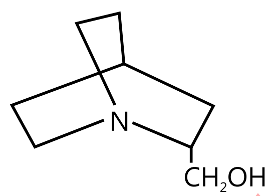
(B) P can not give effervescence of CO_2 with $NaOH_3$.

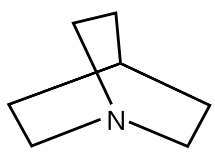
(C) It is Dieckmann condensation

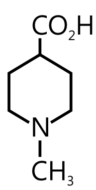
(D) Product is a bicylo compound

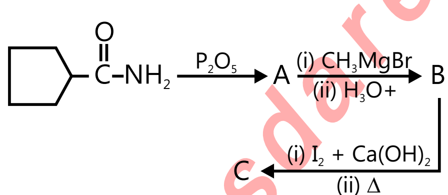
Q.14 

(A) 

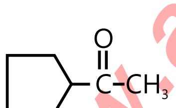
(B) 

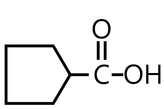
(C) 

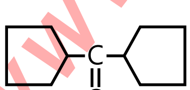
(D) 

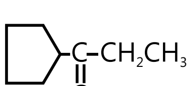
Q.15 

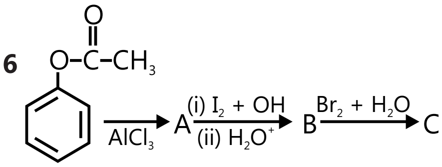
Product is:

(A) 

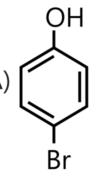
(B) 

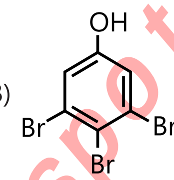
(C) 

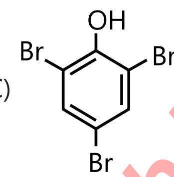
(D) 

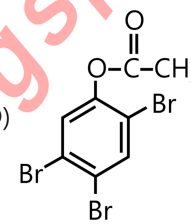
Q.16 

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

(A) 

(B) 

(C) 

(D) 

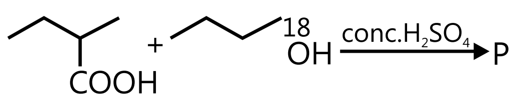
Q.17 Which of the following esters cannot undergo self Claisen condensation

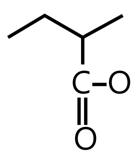
(A) $CH_3CH_2CH_2CH_2CO_2C_2H_5$

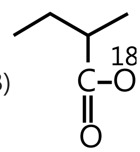
(B) $C_6H_5CO_2C_2H_5$

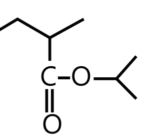
(C) $C_6H_5CH_2CO_2C_2H_5$

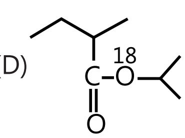
(D) $CH_3CH_2CO_2C_2H_5$

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)***

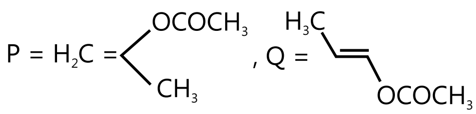
(A) Methyl group (B) Carboxylic acid group

(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

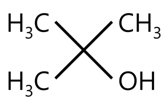
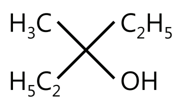
Q.3 The product of acid hydrolysis of P and Q can be distinguished by ***(2003)***

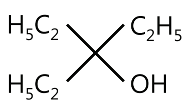
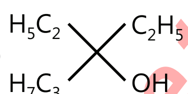


(A) Lucas reagent (B) 2,4-DNP

(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)***

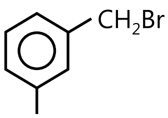
(A) Tollen's reagent (B) Molisch reagent

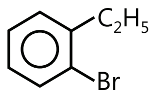
(C) Neutral $FeCl_3$ (D) Aqueous NaOH

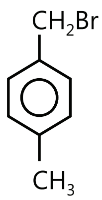
Q.15 A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is: ***(2013)***

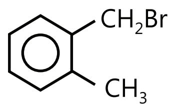
(A) 2 (B) 5 (C) 4 (D) 6

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)***

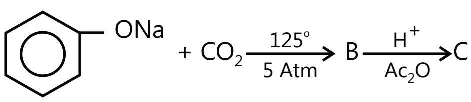
(A) CH_3COOH

(B) $CH_3CH_2CH_2COOH$

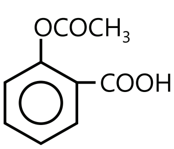
(C) $CH_3-\underset{\underset{CH_3}{|}}{CH}-COOH$

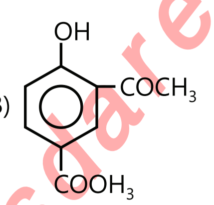
(D) CH_3CH_2COOH

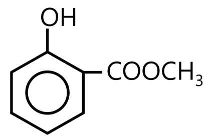
Q.18 Sodium phenoxide when heated with CO_2 under pressure at 125°C yields a product which on acetylation produces C.

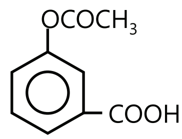


The major product C would be ***(2014)***

(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:

$$\text{Acetylene} + CH_3MgBr \xrightarrow[-CH_4]{} (G) \xrightarrow{CO_2} (H)$$

$$(C_3H_4O_3)\,(J) \xleftarrow[HgSO_4]{H_2O,H_2SO_4} (C_3H_2O_2)(I) \xleftarrow{H_2O} (H)$$

$$(J) \xrightarrow{KMnO_4} CH_2(COOH)_2$$

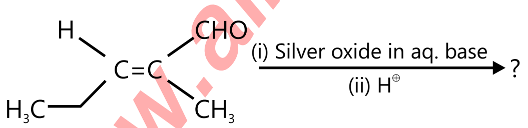
Q.4 An ester $C_6H_{12}O_2$ was hydrolysed with water an acid (A), and an alcohol (B), were obtained. Oxidation of (B) with chromic acid produced A. What is the structure of the original ester? Write equations for all the reactions.

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 $-\overset{\overset{\large O}{\|}}{C}-$ 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

$$\underset{CH}{\overset{CH}{|||}} \xrightarrow{X} \overset{CH_3}{\underset{}{|}}\!\!CHO \xrightarrow{Y} \overset{CH_3}{|}\!\!COOH \xrightarrow{Z} CH_4$$

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?

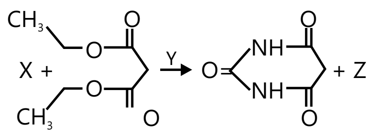
(i) Acetyl chloride from methyl chloride

(ii) Acetamide from ethyl alcohol

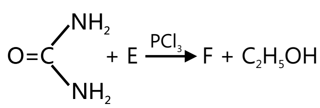
(iii) Ethyl acetate from acetic acid

Q.20 Complete the following reaction?

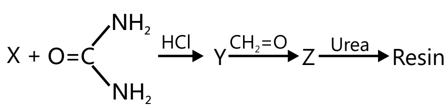
(i)



(ii)



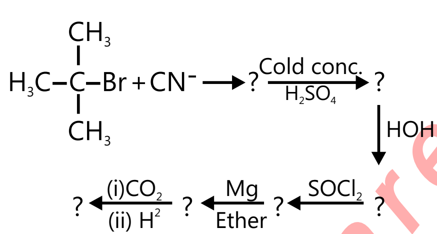
(iii)



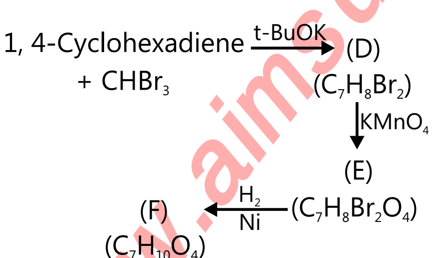
Q.21 Complete the following equations:

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

(ii)



Q.22 Identify the compounds:



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.

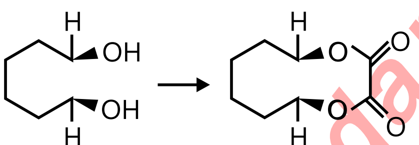
Q.29 An organic compound A on treatment with ethyl alcohol gives a carboxylic acid B and compound C. Hydrolysis of C under acidic conditions gives B and D. Oxidation of D with $KMnO_4$ also gives B. The compound B on heating with $Ca(OH)_2$ gives E (molecular formula C_3H_6O). E does not give Tollen's 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.

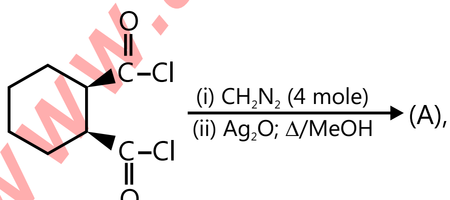


(A) $ClCOCH_2–CH_2\ COCl$

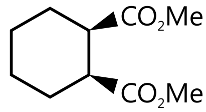
(B) $CH_3COOCOCH_3$

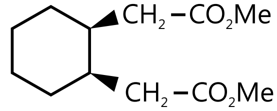
(C) $CH_3\ COCl$

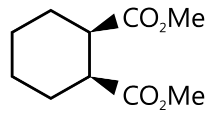
(D) ClCOCOCl

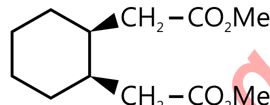
Q.2 

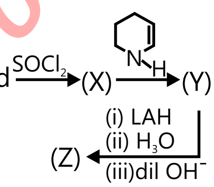
Product (A) of reaction is ?

(A) 

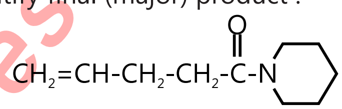
(B) 

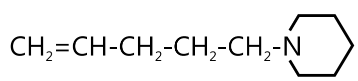
(C) 

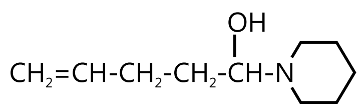
(D) 

Q.3 4-Pentenoic acid 

Identify final (major) product :

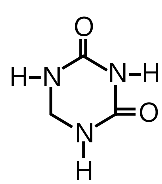
(A) 

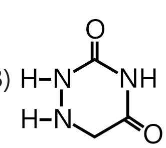
(B) 

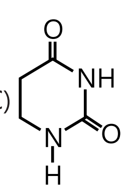
(C) 

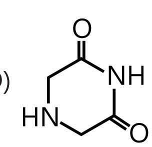
(D) $CH_3–CH_2–CH_2–CH_2–CH_2–OH$

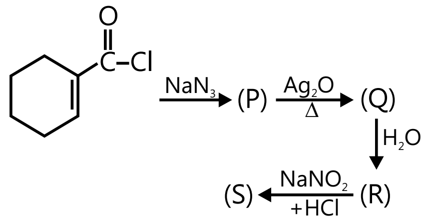
Q.4 $H_2N-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-N_3 \xrightarrow{\Delta} P$; P is :

(A) 

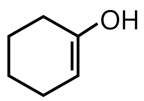
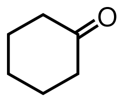
(B) 

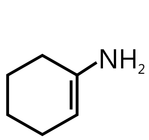
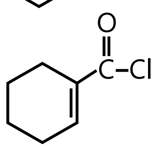
(C) 

(D) 

Q.5 

Identify (S) major product:

(A)  (B) 

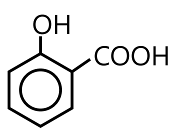
(C)  (D) 

Multiple Correct Choice Type

Q.6 Which will elimination CO_2 only on heating

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

(B) $Ph-\underset{\underset{O}{\|}}{C}-CH_2-SO_3H$

(C) 

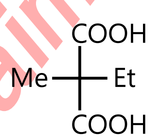
(D) $CH_2=CH-CH_2-COOH$

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.

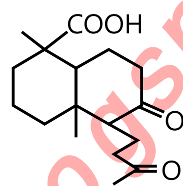
(B) Statement-I is true, Statement-II is true and Statement-II is NOT the correct explanation for Statement-I.

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

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

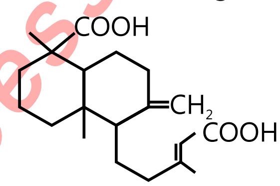
Comprehension Type

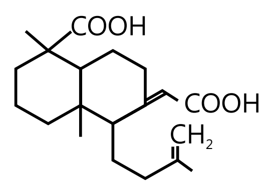
Paragraph 1: Ozonolysis of a compound Agathene dicarboxylic acid gives following compounds:

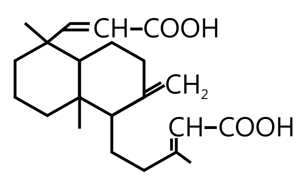
HCHO, $\underset{COOH}{\underset{|}{CHO}}$ & 

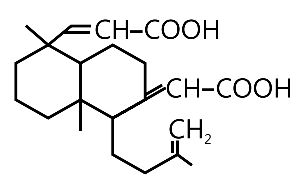
On complete reaction by Na-EtOH Agathene dicarboxylic acid give hydrocarbon $C_{20}H_{38}$ which have 5 chiral carbon in it.

Q.9 The structure of Agathene dicarboxylic acid is:

(A) 

(B) 

(C) 

(D) 

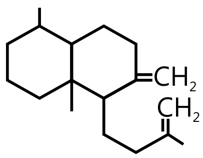
Q.10 How many chiral carbon are present in Agathene dicarboxylic acid:

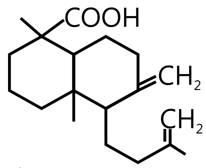
(A) 2 (B) 3 (C) 4 (D) 5

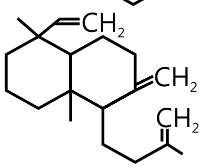
Q.11 Total stereoisomers possible for Agathene dicarboxylic acid are :

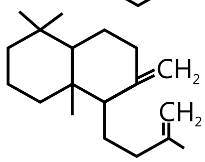
(A) 16 (B) 18 (C) 32 (D) 64

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

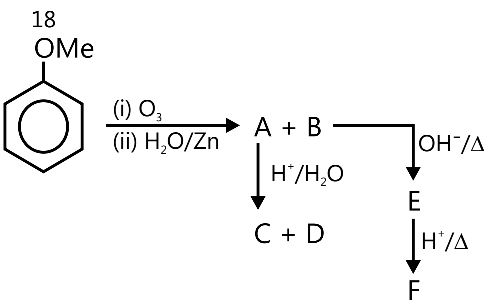
(A) 

(B) 

(C) 

(D) 

Paragraph 2:



Q.13 Product C and D are :

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

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

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

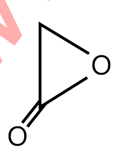
(D) $HO-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH+Me\overset{18}{O}H$

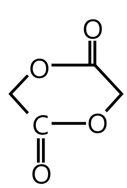
Q.14 Mechanism for hydrolysis of A will be:

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

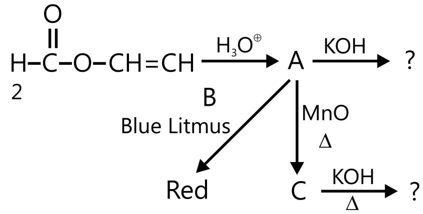
Q.15 F is

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

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

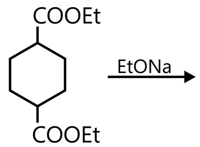
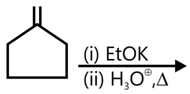
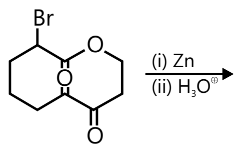
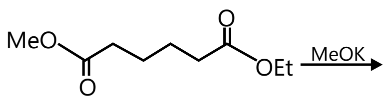
(B) $H-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{Me_2Cd}$

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

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

Match the Columns

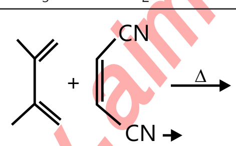
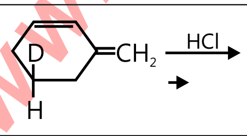
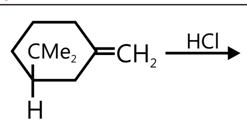
Q.22 Match reactions given in column I with Names in column II.

Column I		Column II	
(A)		(p)	Knoevenagel reaction
(B)	$CH_2(COOEt)_2$ + 	(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)	$CH_3-\overset{\overset{CH_3}{\vert}}{C}=CH-CH_3 \xrightarrow[Zn]{O_3} (W)+(X)$	(q)	By Fehling test
(C)	$Ph-\overset{\overset{O}{\Vert}}{C}-O-Ph \xrightarrow{H_3O^{\oplus}} (Y)+(Z)$	(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)	$CH_3-\underset{\underset{O}{\parallel}}{C}-H \xrightarrow[\text{(ii) } H_3O^{\oplus}]{\text{(i) } Al(OEt)_3,\Delta}$ Products	(p)	One of the organic product formed will decolourise bromine water
(B)	$C_6H_5-\underset{\underset{O}{\parallel}}{C}-H + CH_2(COOMe)_2 \xrightarrow[\text{(ii) } H_3O^{\oplus}/\Delta]{\text{(i) } MeO}$ Product(s)	(q)	One of the organic product formed will give brisk effervescence with $NaHCO_3$
(C)	$PhMgCl \xrightarrow[\text{(ii) } H^{\oplus} \text{ (iii) } SOCl_2 \text{ (iv) } MeMgCl]{\text{(i) } CO_2}$ 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)	$R'-CH_2-Br \xrightarrow{\text{LAH}}$	(r)	$R'-CH_2-OH$
(D)	$R'-\underset{\underset{O}{\parallel}}{C}-H \xrightarrow{\text{SBH/EtOH}}$	(s)	$R'-H$
(E)	$R-\underset{\underset{O}{\parallel}}{C}-OR' \xrightarrow{\text{Red P/HI}}$	(t)	$R-CH_3$

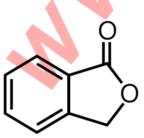
Previous Years' Questions

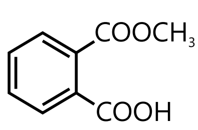
Q.1 When benzene sulphonic acid and p–nitrophenol are treated with $NaHCO_3$, the gases released respectively, are ***(2006)***

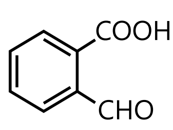
(A) SO_2, NO_2 (B) SO_2, NO

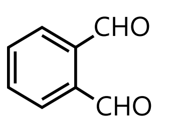
(C) SO_2, CO_2 (D) CO_2, CO_2

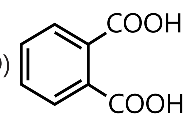
Q.2 Which of the following reactants on reaction with conc. NaOH followed by acidification gives the following lactone as the only product? ***(2006)***



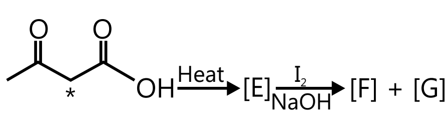
(A) 

(B) 

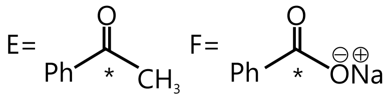
(C) 

(D) 

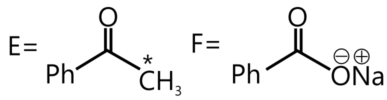
Q.3 In the following reaction sequence, the correct structures of E, F and G are



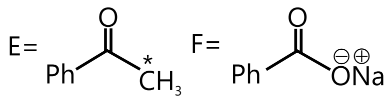
(* implies ^{13}C labelled carbon) ***(2008)***

(A) 

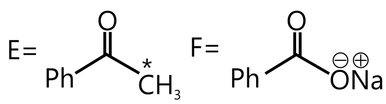
G=CHI_3

(B) 

G=CHI_3

(C) 

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

(D) 

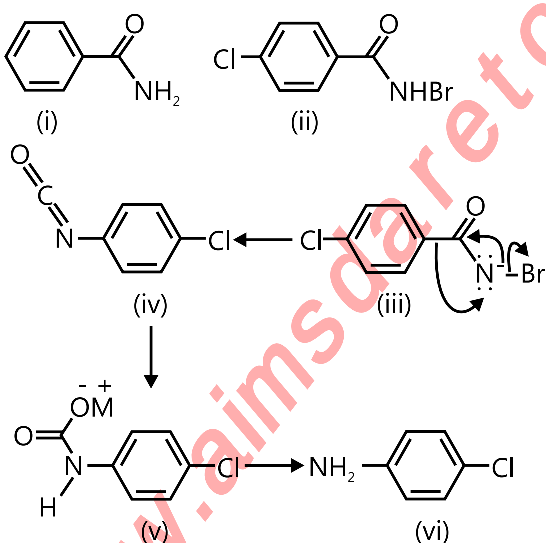
G=$\overset{*}{C}H_3I$

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

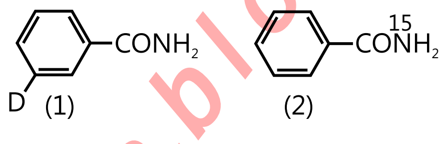
(C) KBr + KOH (D) Br_2 + KOH

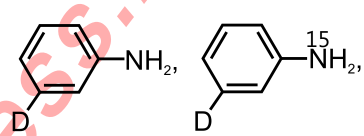
Q.6 Which is the determining step in Hofmann bromamide degradation ?

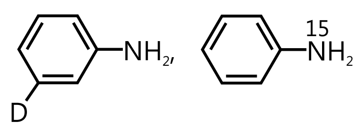
(A) Formation of (i) (B) Formation of (ii)

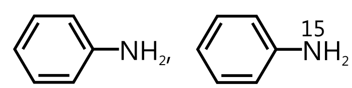
(C) Formation of (iii) (D) Formation of (iv)

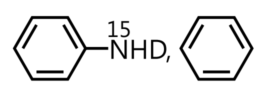
Q.7 What are the constituent amine formed when the mixture of (1) and (2) undergoes Hofmann bromamide degradation ?



(A) 

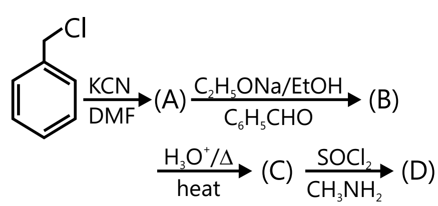
(B) 

(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)***

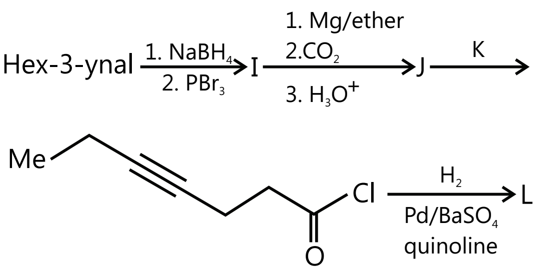
Q.9 Compound A of molecular formula $C_9H_7O_2Cl$ exists in keto from and predominantly in enolic form B. On oxidation with $KMnO_4$, A gives m-chlorobenzoic acid. Identify A and B. ***(2003)***

Q.10 

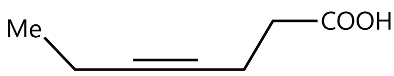
Identify A to D. ***(2004)***

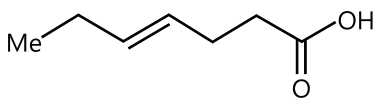
Paragraph 1 (Questions 11 to 12)

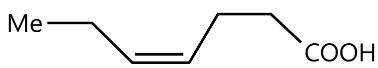
In the following sequence, products I, J and L are formed. K represents a reagent.



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

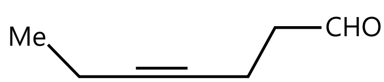
(A)  and $SOCl_2$

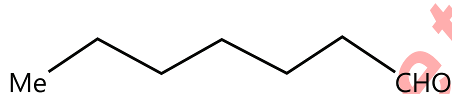
(B)  and $SOCl_2$

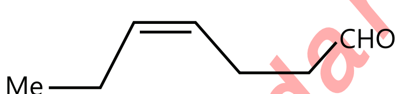
(C)  and $SOCl_2$

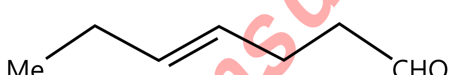
(D)  and CH_3SO_2Cl

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

(A) 

(B) 

(C) 

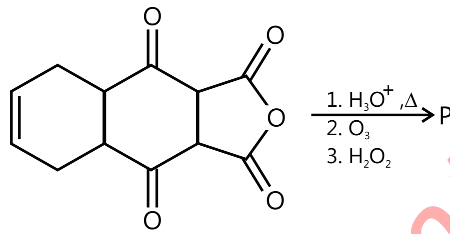
(D) 

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

(A) Picric acid (B) Barbituric acid

(C) Ascorbic acid (D) Aspirin

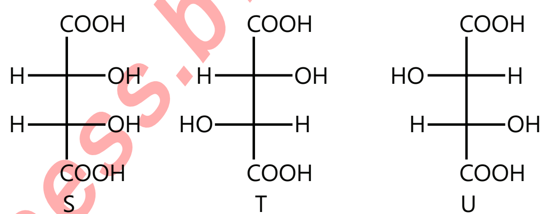
Q.14 The total number of carboxylic acid groups in the product P is: ***(2013)***



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.



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

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

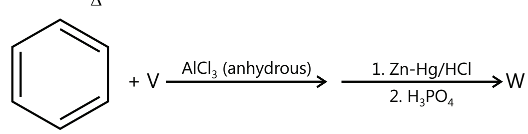
(B) Optically inactive S and optically inactive pair (T, U)

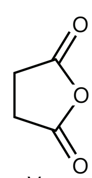
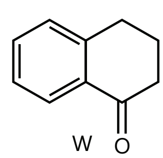
(C) Optically active pair (T, U) and optically active S

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

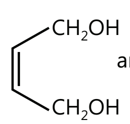
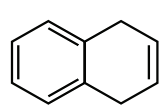
Q.16 In the following reaction sequences V and W are, respectively ***(2013)***

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

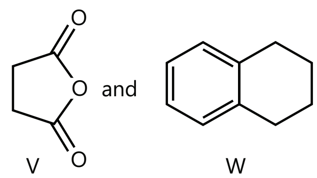


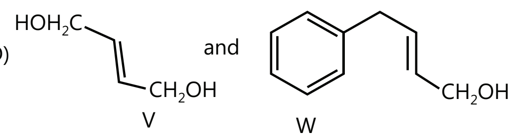
(A)  and 

V

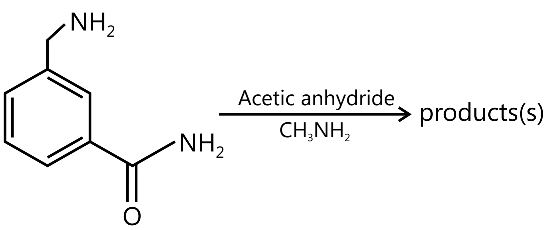
(B)  and 

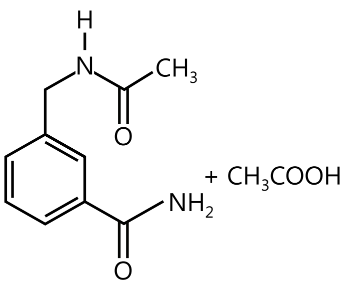
V W

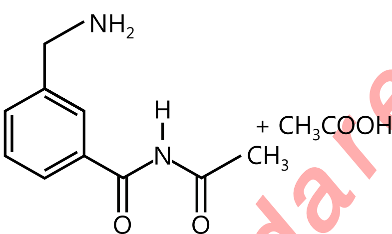
(C) 

(D) 

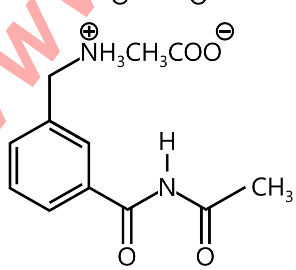
Q.17 In the reaction shown below, the major product(s) formed is/are ***(2014)***



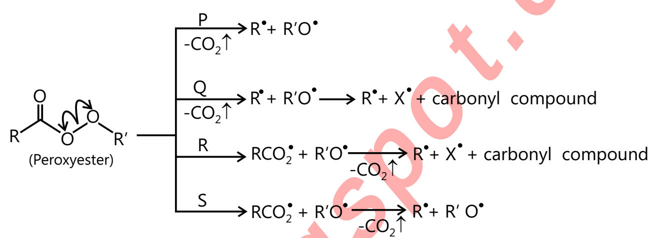
(A) 

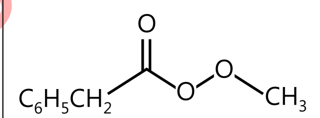
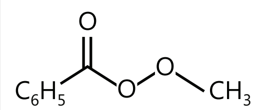
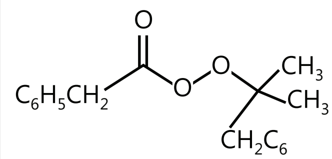
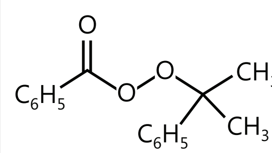
(B) 

(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)***

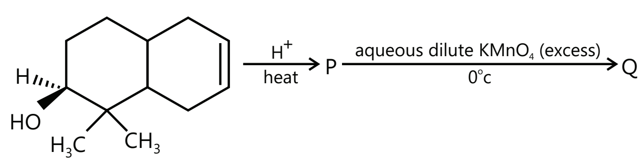


	List I		**List II**
(i)	Pathway P	(p)	
(ii)	Pathway Q	(q)	
(iii)	Pathway R	(r)	
(iv)	Pathway S	(s)	

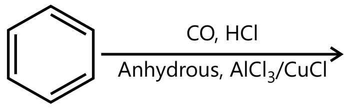
Code:

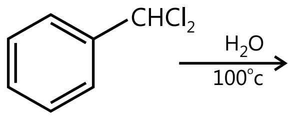
	(i)	(ii)	(iii)	(iv)
(A)	p	r	s	q
(B)	q	s	r	p
(C)	s	p	q	r
(D)	r	q	p	s

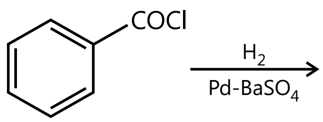
Q.19 The number of hydroxyl group(s) in Q is ***(2015)***

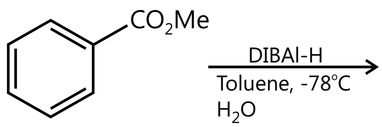


Q.20 Among the following, the number of reaction(s) that produce(s) benzaldehyde is ***(2015)***

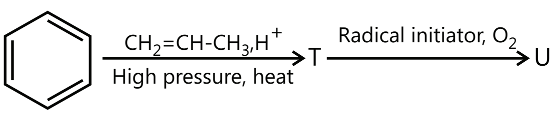
(A) 

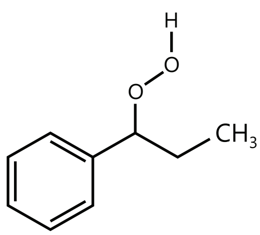
(B) 

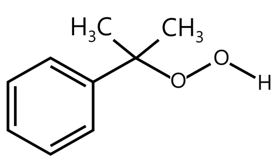
(C) 

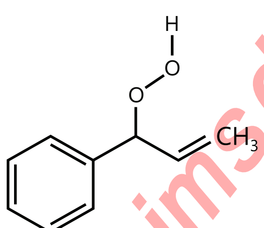
(D) 

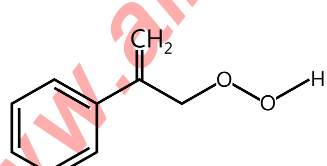
Q.21 The major product U in the following reactions is ***(2015)***



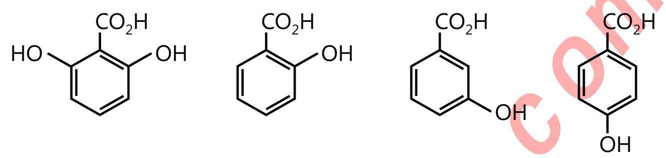
(A) 

(B) 

(C) 

(D) 

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

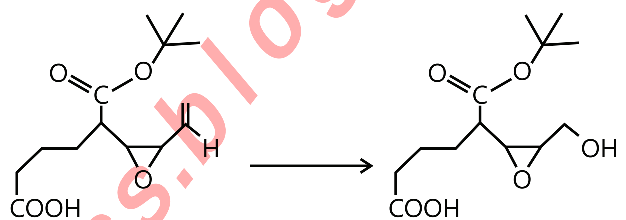


(I) (II) (III) (IV)

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

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

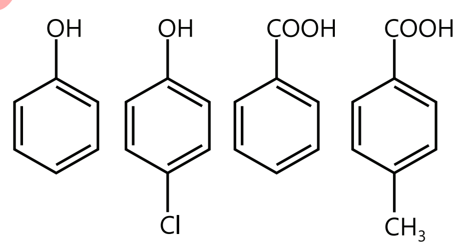
Q.23 Reagent(s) which can be used to bring about the following transformation is(are) **(2016)**



(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)***

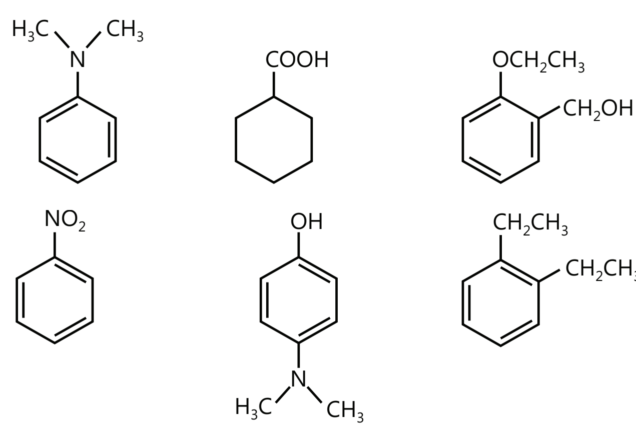


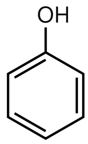
(I) (II) (III) (IV)

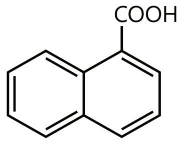
(A) (III) > (IV) > (II) > (I) (B) (IV) > (III) > (I) > (II)

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

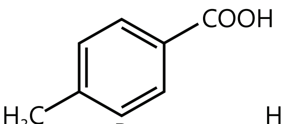
Q.25 Amongst the following, the total number of compounds soluble in aqueous NaOH is : ***(2010)***

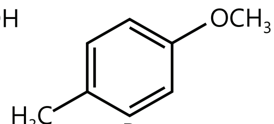


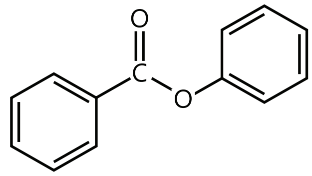




Q.26 The compounds P, Q and S ***(2010)***

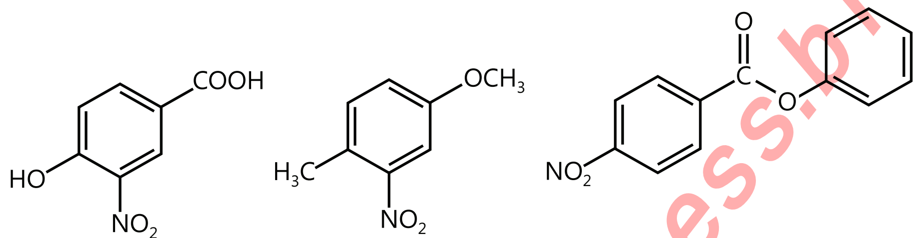

P


P

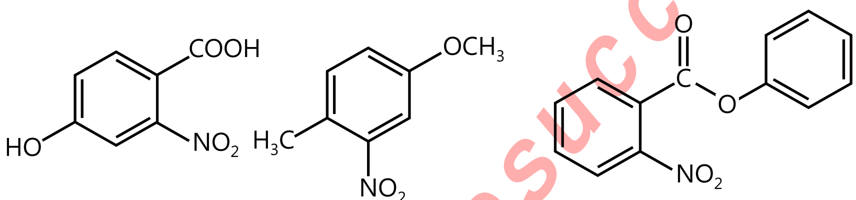

S

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

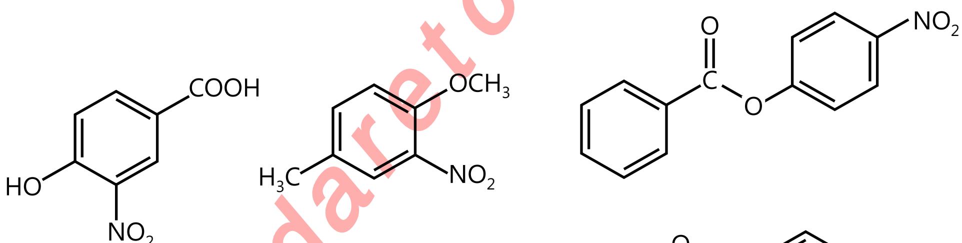
(A)



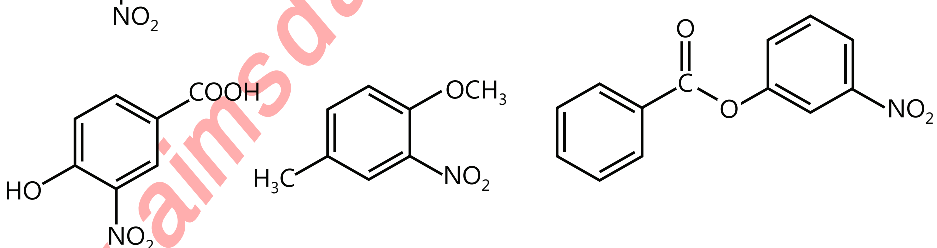
(B)



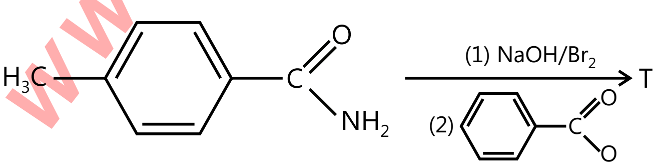
(C)

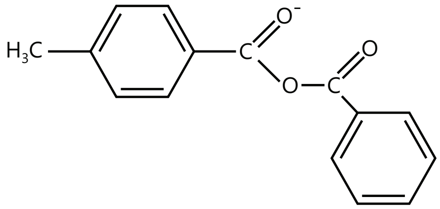


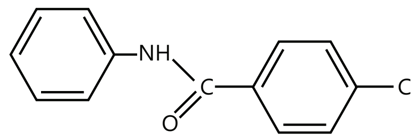
(D)

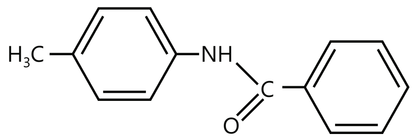


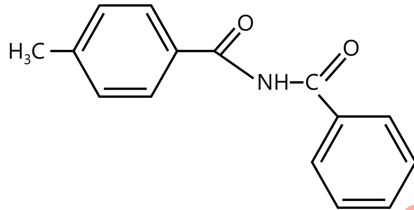
Q.27 ***(2010)***



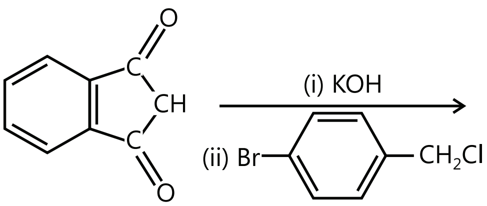
(A) 

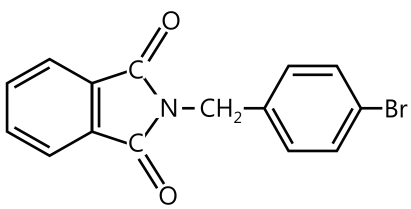
(B) 

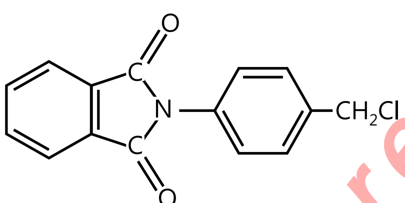
(C) 

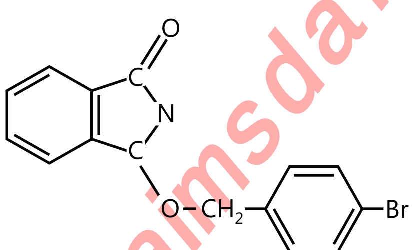
(D) 

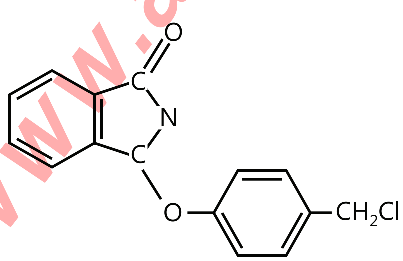
Q.28 The major product of the following reaction is ***(2011)***



(A) 

(B) 

(C) 

(D) 

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

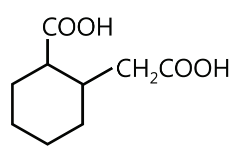
(A) p-nitrophenol

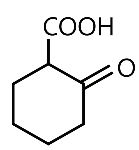
(B) p-hydroxybenzoic acid

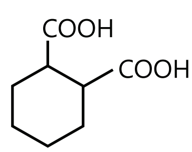
(C) o-hydroxybenzoic acid

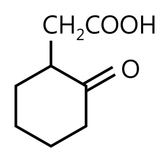
(D) p-toluic acid

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

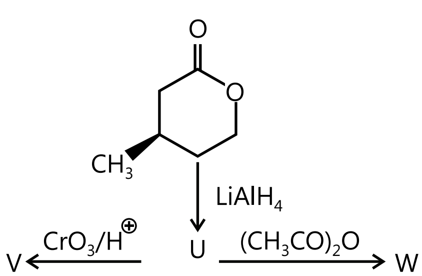
(A) 

(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. $NaHCO_3$

PlancEssential 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 $\rightarrow$ s; B $\rightarrow$ p; C $\rightarrow$ r; D $\rightarrow$ s

Q.20 A $\rightarrow$ p; B $\rightarrow$ q, s; C $\rightarrow$ r

Q.21 A $\rightarrow$ p; B $\rightarrow$ r, t; C $\rightarrow$ p, s; D $\rightarrow$ p, q, s

Q.22 A $\rightarrow$ q, r; B $\rightarrow$ p, q; C $\rightarrow$ r, s

Q.23 A $\rightarrow$ q, ; B $\rightarrow$ r; C $\rightarrow$ p; D $\rightarrow$ r; E $\rightarrow$ 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

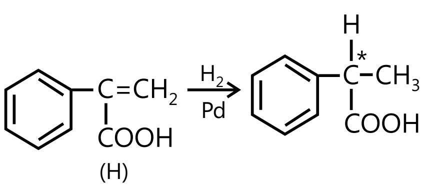
Sol 1: The uptake of 2H atoms shows the presence of one >C=C< along with C_6H_5- and –COOH, which accounts for the 6° unsaturation.. Furthermore H and I are monosubstituted benzene derivatives.

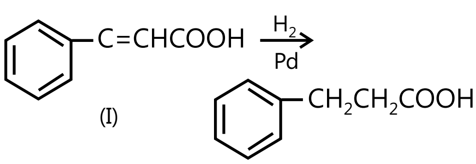
H is $C_6H_5-C(COOH)=CH_2$ giving

$H_3CCHC_6H_5COOH$ with one asymmetric carbon atom.

I is $C_6H_5CH=CHCOOH$, giving

$C_6H_5CH_2CH_2COOH$ with no asymmetric carbon.





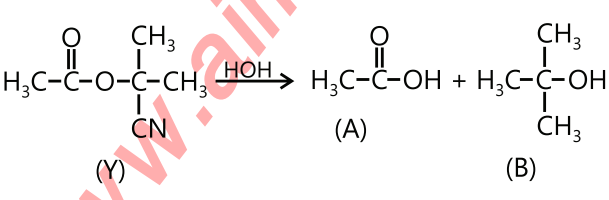
Sol 2: (A) = $C_{15}H_{31}CH_2OH$,

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

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

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

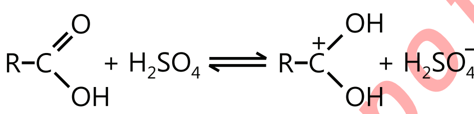
Sol 3: (Y) is an ester because it is hydrolysed to acid and alcohol. Since the alcohol is not oxidized by acidified $KMnO_4$ and gives cloudiness at once with Lucas reagent, hence it is a t-alcohol.



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.

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

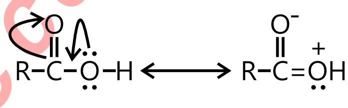
Sol 5: In the presence of strong acids, the $H^{\oplus}$ is captured by the carboxylic acid and the following equilibrium is established:



Sol 6: $H_3C-CH_2CH_2\overset{\overset{O}{\|}}{C}-CH_3$

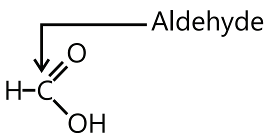
Sol 7: It is because the carboxylate group ($-COO^-$) of the branched acid is more shielded from the solvent molecules, there, it cannot be stabilized effectively by salvation.

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.



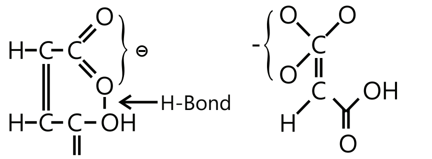
Hence it has reducing character of aldehydes.

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

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

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:

$CH_3-CH_2-MgBr \xrightarrow{H_3C-CH_2 \text{ (epoxide)}}$

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

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

$CH_3CH_2-CH_2COOH$
(Z) Butanoic acid

Sol 12:

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

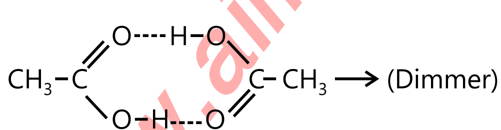
$CH_3-C{\equiv}C-CH_3 \xrightarrow[HgSO_4]{H_2SO_4} CH_3-\underset{\underset{OH}{|}}{C}=CH-CH_3$

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

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

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

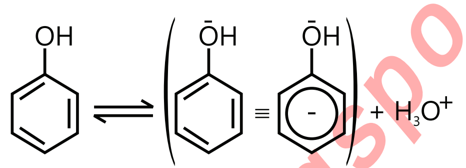
Sol 13:

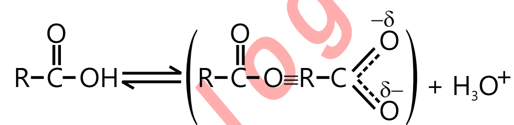


Dimerization of acetic acid occur in benzene via intermolecular H-bonding Hydrogen bond is a special type of dipole-attraction.

Sol 14: sp hybridized carbon of $-C{\equiv}C-$ of acid (I) and sp^2 hybridized carbon of $-C{=}C-$ of acid (II) attract the bonded electron more than do the sp^3 – hybridzed carbon atoms. Consequently $-C \equiv C-$ and $-C \equiv C-$ 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 $-C \equiv C-$ is more acid strengthens group than $-C \equiv C-$ 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 = Equiva lent 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

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

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

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

Sol 20: As the size of the substituent on α-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) $CH_3CH_2CO\underset{\displaystyle CH_3}{\underset{|}{C}}HCOOC_2H_5$

Ethyl-(3-keto 2-methylpentanoic acid)

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

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)

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

Cis Trans

(B) $CH_3CH_2-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{}^*-COOH$

(2-methylbutanoic acid)

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

Sol 26: A = CH_3OH (Methanol)

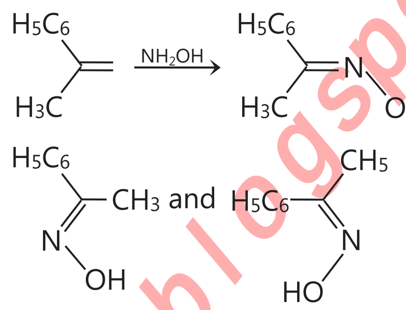
B = CH_3COCH_3 (Methyl ethanoate)

C = HCHO (Methanal)

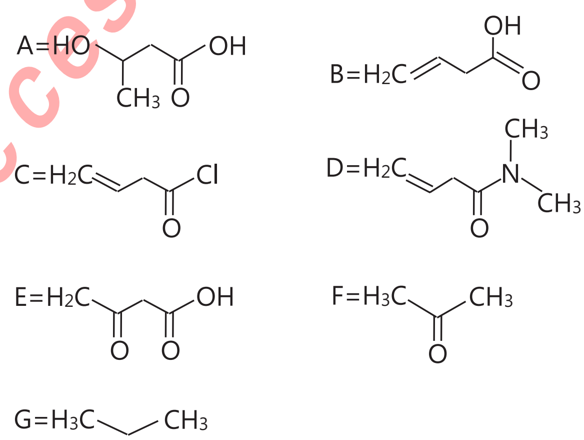
D = HCOOH (Methanoic acid)

E = $HCONH_2$ (Formamide or methanamide)

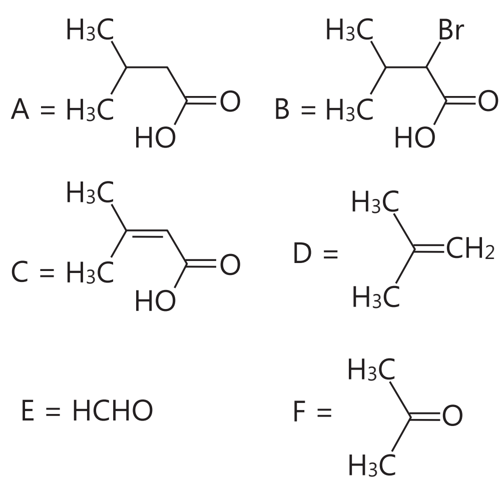
Sol 27:



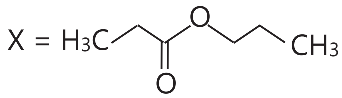
Sol 28:



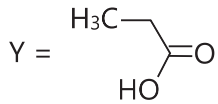
Sol 29:



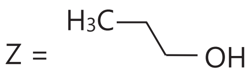
Sol 30:



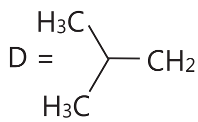
Propyl propionate



Propionic acid



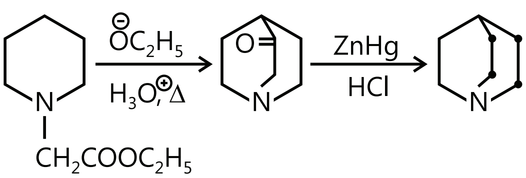
Propan-1-ol



Exercise 2

Single Correct Choice Type

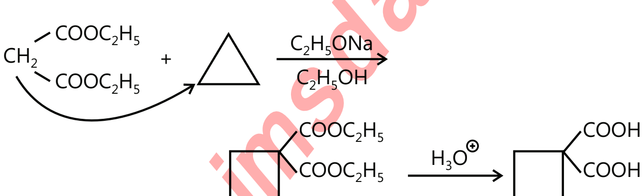
Sol 1: (B)



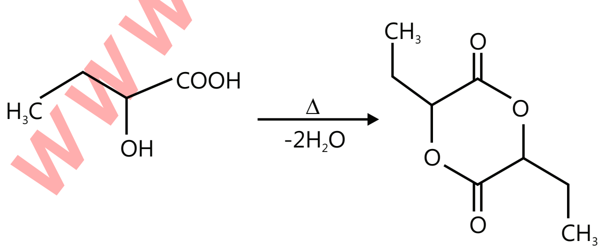
Sol 2: **(A)** MeCOCl > $MeCON_3$ > MeCOOCOMe. Consider electronegativity of halogen, azide & ester.

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

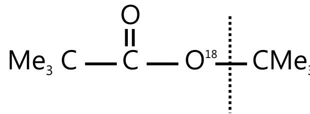
Sol 3: (D)



Sol 4: (C)



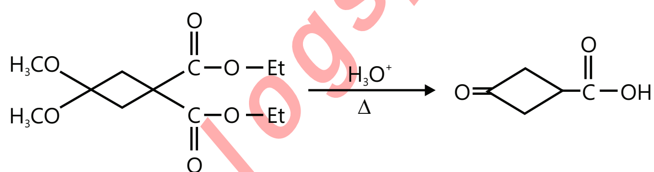
Sol 5: (B) Acid catalyzed alkyl cleavage



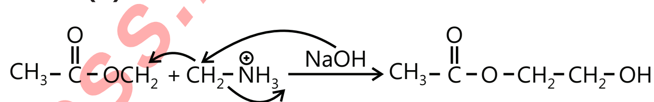
Sol 6: (A)

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

Sol 7: (B)

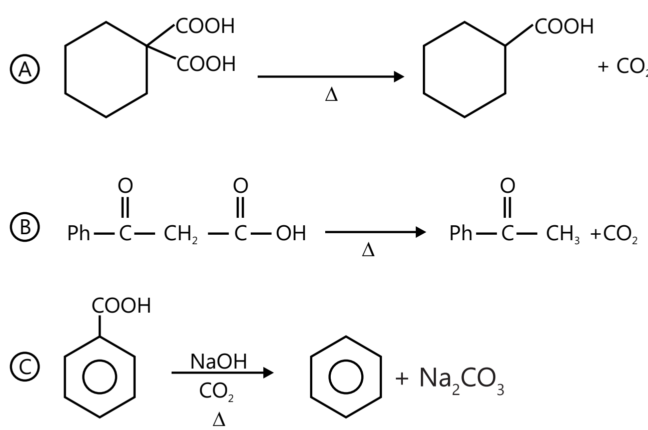


Sol 8: (B)

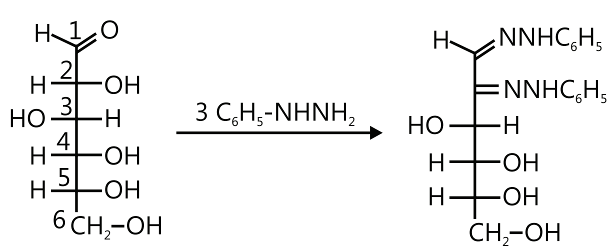


Sol 9: (D) Reduction reactions.

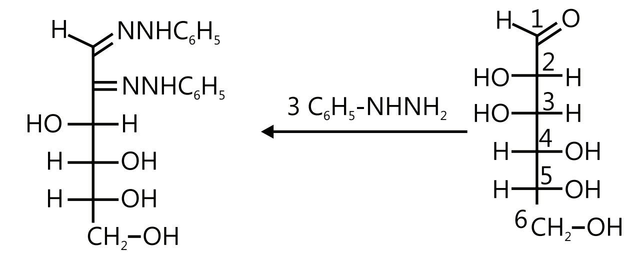
Sol 10: (D)



Sol 11: (B)



D-(+)-glucose　　　common D-osazone



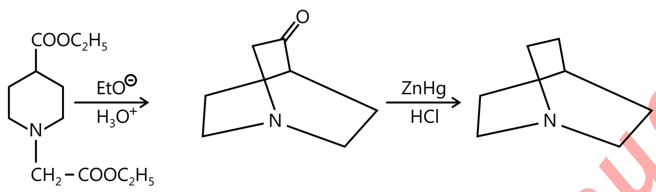
common D-osazone D-(+)-mannose

Sol 12: (A) Esterification.

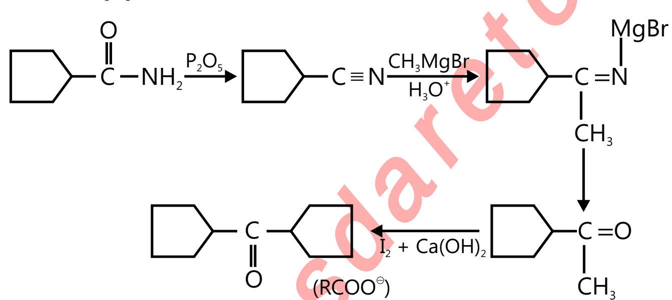
$$Ph-\overset{O}{\overset{\|}{C}}-O-H+HO^{18}CH(CH_3)_2 \xrightarrow[\Delta]{HCl} Ph-\overset{O}{\overset{\|}{C}}-O^{18}-CH(CH_3)_2$$

Sol 13: (B) Dieckmann condensation product.

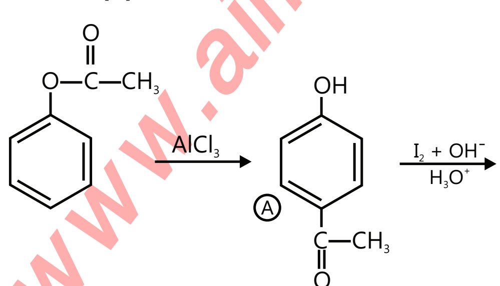
Sol 14: (C)

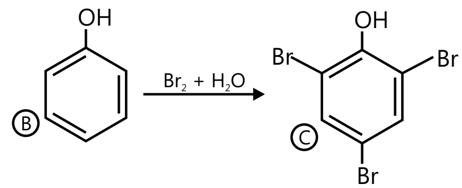


Sol 15: (C)



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)

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

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

Sol 4: (A)

$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[\text{excess}]{CH_3MgBr} CH_3-\overset{OMgBr}{\underset{CH_3}{C}}-CH_3 \xrightarrow{H_2O} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$$

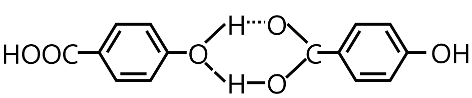
Sol 5: (D) $R-\overset{\overset{O}{\|}}{C}-OH + H-OR' \xrightarrow{-H^+} R-\underset{\underset{OR'}{|}}{\overset{\overset{O^-}{|}}{C}}-OH$

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

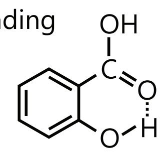
Sol 6: (B) $C_6H_5-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{POCl_3} C_6H_5-CN$

Sol 7: (C) Compound with $CH_3-\overset{\overset{O}{\|}}{C}-$ 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 α-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)

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

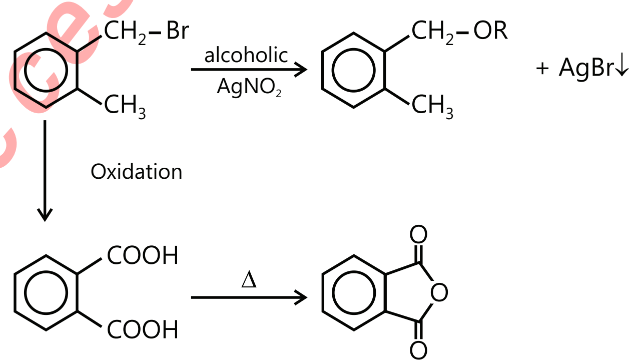
K_a of $HC_3CH_2CH_2\underset{\underset{Cl}{|}}{C}H-COOH$ is 139×10^{-5}

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

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

Sol 16: (D)



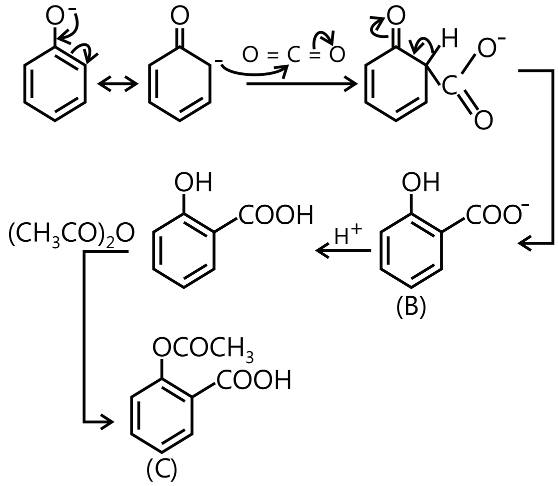
(Phthalic anhydride)

Sol 17: (D)

$$\underset{(A)}{CH_3CH_2-\overset{\overset{O}{\|}}{C}-OH} \xrightarrow{NH_3} \underset{(B)}{CH_3CH_2CO\overset{-}{O}\overset{\oplus}{N}H_4}$$

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

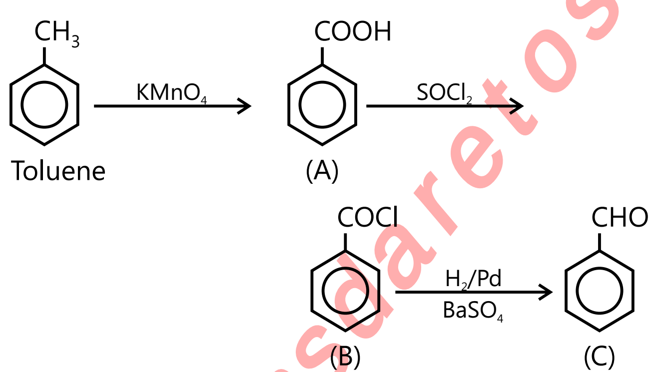
Sol 18: (A)



Sol 19: (C)

$$CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \quad \text{'A'}$$
$$\downarrow PCl_5$$
$$CH_3CH_2Cl \quad \text{'B'}$$
$$\downarrow \text{Alc.KOH}$$
$$CH_2{=}CH_2 \quad \text{'C'}$$

Sol 20: (D)



Sol 21: (C) Hofmann bromamide degradation reaction

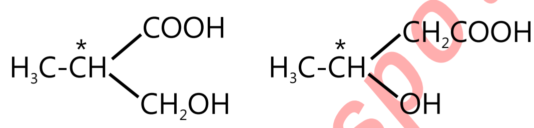
$$R-\overset{\overset{\large O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow$$
$$R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

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

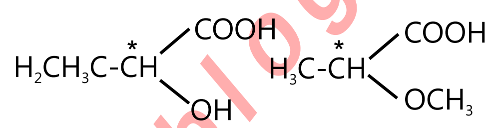
JEE Advanced/Boards

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.

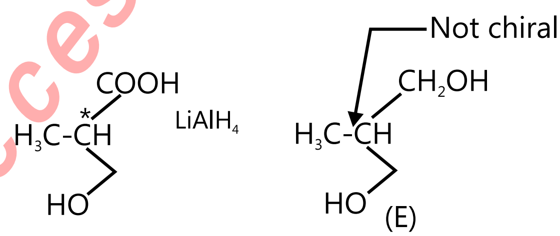


(D) (E)



(F) (G)

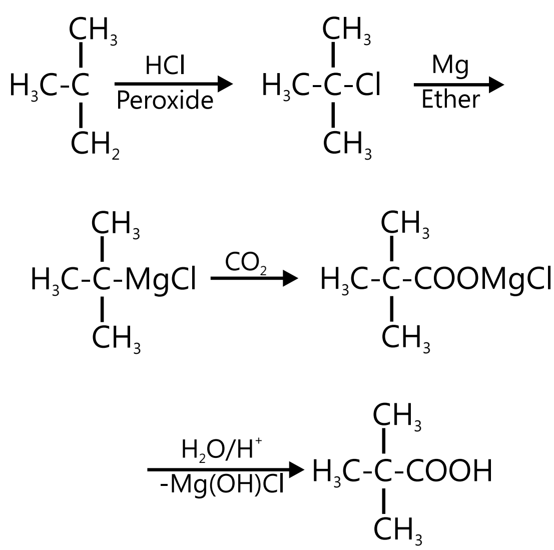
(ii) $LiAlH_4$ converts–COOH to $-CH_2OH$. Only (D) is reduced to an a chiral product.



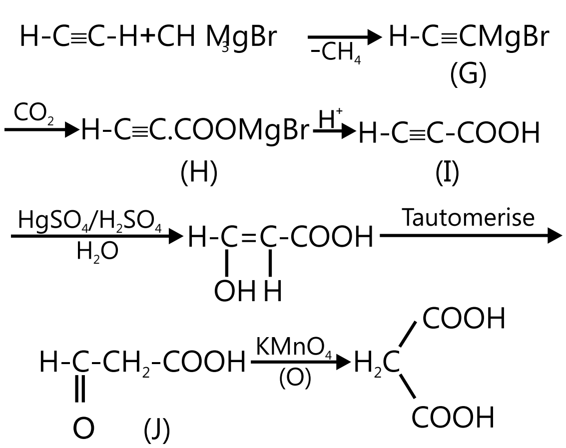
(D)

(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:



Sol 3:



Sol 4:

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

$$\underset{(A)}{CH_3CH_2COOH} + \underset{(B)}{CH_3CH_2CH_2OH}$$

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

$$CH_2CHO \xrightarrow{(O)} \underset{(A)}{CH_3CH_2COOH}$$

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

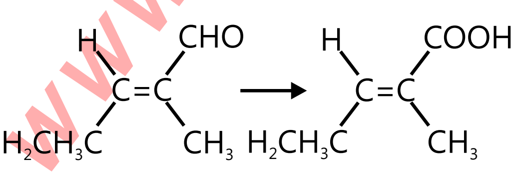
$RCON_3 \xrightarrow{D} RNCO \xrightarrow{\text{Hydrolysis}} RNH_2$

Sol 6: C≡O bond is very stable due to large ΔH_f of CO;

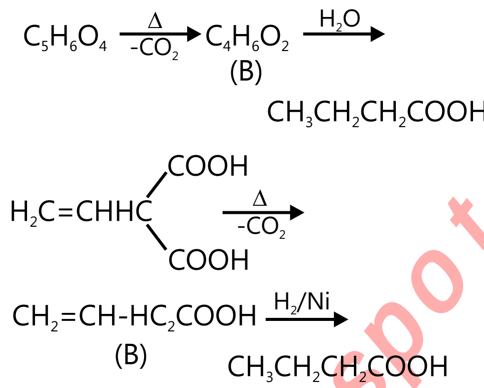
so the decomposition reaction $H-\overset{O}{\overset{\|}{C}}-C \longrightarrow C{\equiv}O + HCl$

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:



Sol 9:

(A) $(CH_3CO)_2O$ (B) CH_3COOH

(C) $CH_3COOC_2H_5$ (D) C_2H_5OH

(E) CH_3COCH_3

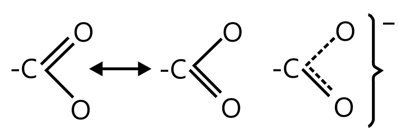
Sol 10: (A) ($C_2H_5COOC_2H5$)

(B) $C_2H_5CO–CH(CH_3)COOC_2H_5$

(C) $C_2H_5COCH(CH_3)COOH$

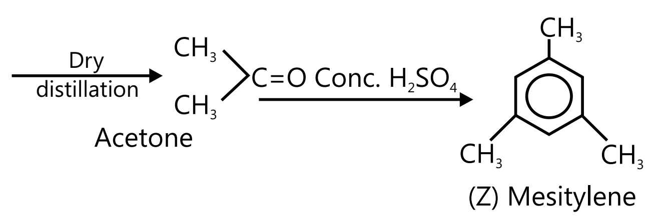
Sol 11: An alkali salt of palmitic acid is known as soap. The general formula of palmitic acid $C_{15}H_{31}COOH$. Which on hydrolysis in presence of alkali give soap($C_{15}H_{31}COONa$) and glycerol as by product.

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: $\underset{(X)}{CH_3COOH} \xrightarrow{Ca(OH)_2} \underset{(Y)}{(CH_3COO)_2Ca}$

Acetic acid Cal. acetate



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.

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

Alkanol

Sol 16:

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

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

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)

$$\underset{(E)}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}\; 2CH_3-\underset{(Y)}{\overset{\overset{\displaystyle O}{\|}}{C}-Cl}$$

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

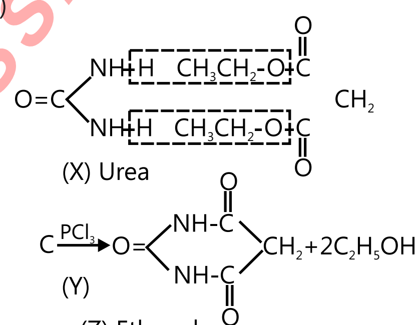
$CH_3COOH \xrightarrow{LiAlH} CH_3CH_2OH$

Acetic acid

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

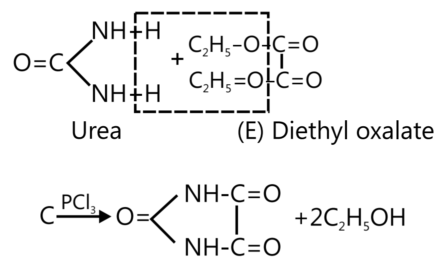
Ethyl acetate

Sol 20: (i)



(X) Urea (Y) (Z) Ethanol

(ii)



Urea (E) Diethyl oxalate

(F) Parabanic acid
(Oxalyl urea)

(iii)

$CH_2{=}O + O{=}C\langle^{NH_2}_{NH_2} \xrightarrow{HCl}$

Formaldehyde (X) Urea

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

Monomethylol urea

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

Dimethylol urea
urea-formaldehyde

Sol 21: (i)

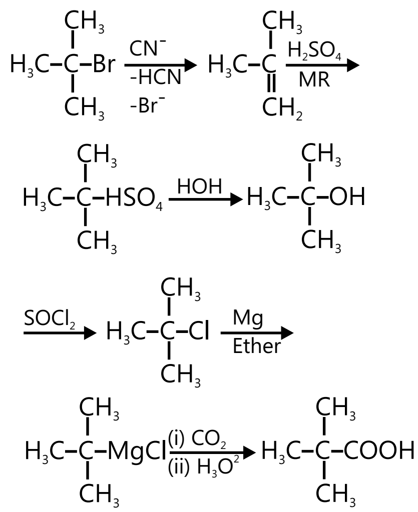
$$CH_3CH_2CH_2CH_2Br \xrightarrow{CN^-}$$

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

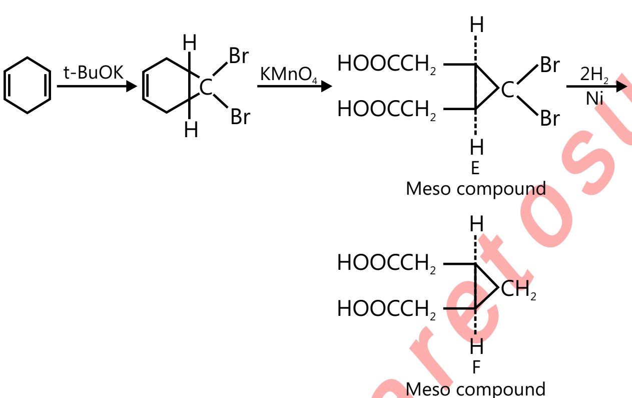
$$CH_3CH_2CH_2CH_2COOH$$

n – Pentanoic acid

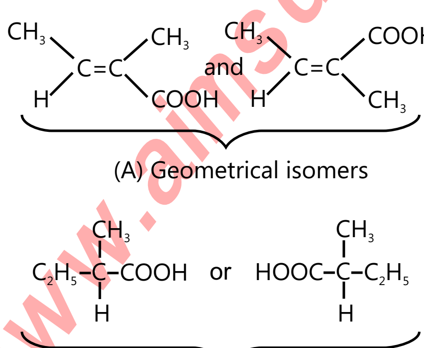
(ii)



Sol 22:



Sol 23:



(A) Geometrical isomers

(B)

Sol 24: (A) $CH_3CHOHCH_2COOH$

(B) $CH_3CH=CHCOOH$

(C) $CH_3CH=CHCOCl$

(D) $CH_3–CH=HCON(CH_3)_2$

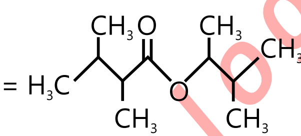
(E) CH_3COCH_2COOH

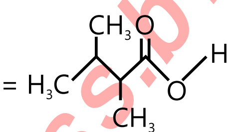
(F) CH_3COCH_3

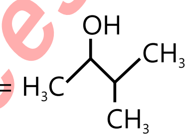
(G) $CH_3CH_2CH_3$

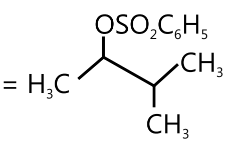
Sol 25: Is a saturated monoester with

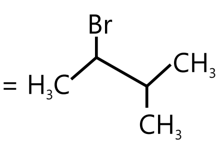
M.W = 186

F = 

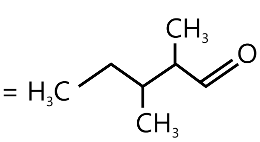
G = 

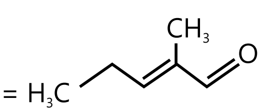
H = 

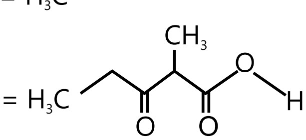
J = 

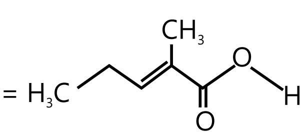
K = 

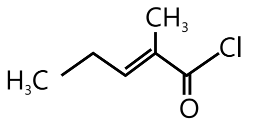
Sol 26:

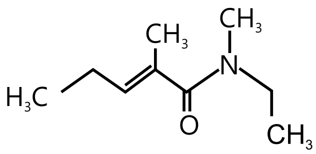
A = 

B = 

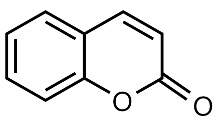
C = 

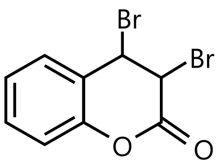
D = 

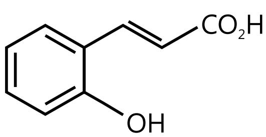
E = 

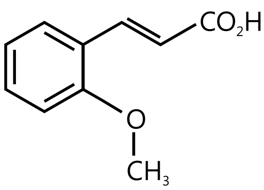
F = 

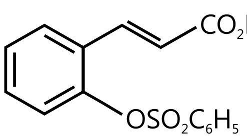
Sol 27:

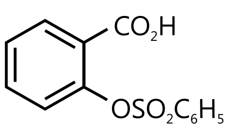
A = 

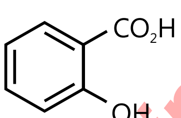
B = 

C = 

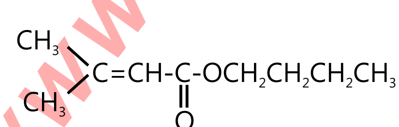
D = 

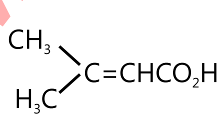
E = 

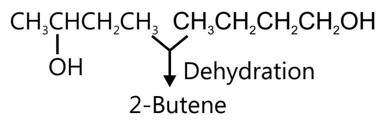
F = 

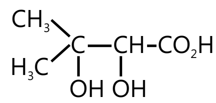
G = 

Sol 28:

(A) 

(B) 

(C) 

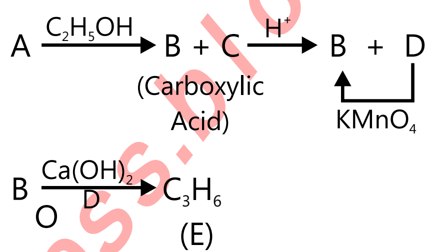
(D) 

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.



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).

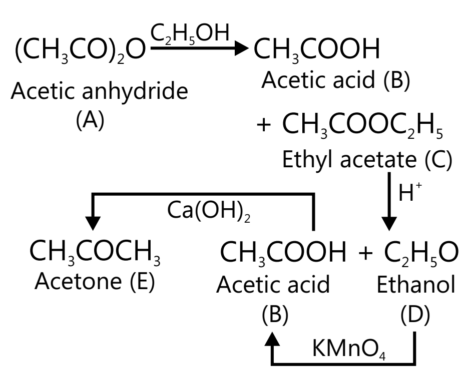
Since E is obtained by heating B with $Ca(OH)_2$, the compound B must be CH_3COOH (acetic acid).

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

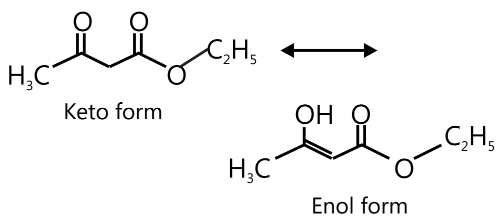
Since B and D are obtained by acid hydrolysis of C, the compound C must be an ester $CH_3COOC_2H_5$(ethyl acetate).

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).

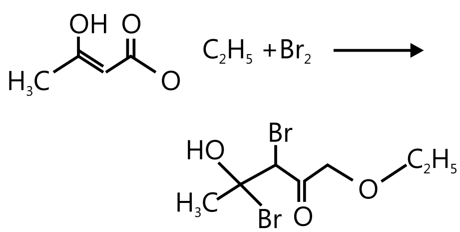
The given reaction are



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.

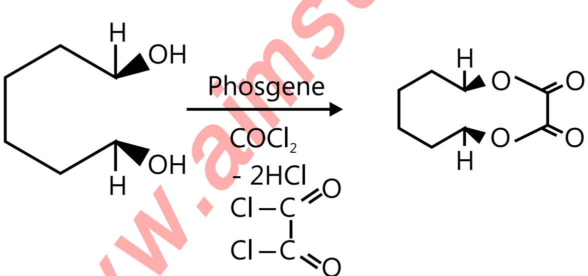


As soon as enol form is consumed, its colouration with $FeCl_3$ disappears and excess of bromine gives brown colour. As keto and enol forms are in equilibrium, when enol form is used, the equilibrium shifts to right hand side to give more enol form which discharges the colour of excess of Br_2 and gives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

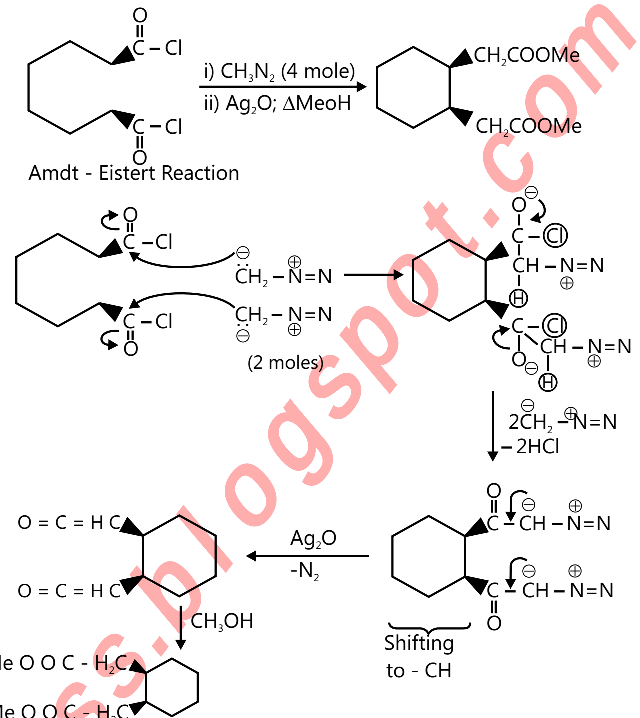
Exercise 2

Single Correct Choice Type

Sol 1: (D)

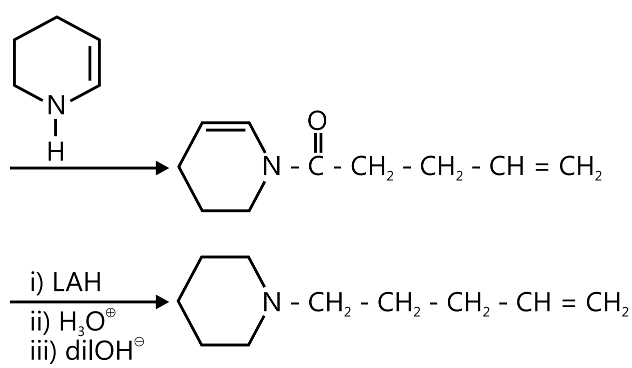


Sol 2: (B)

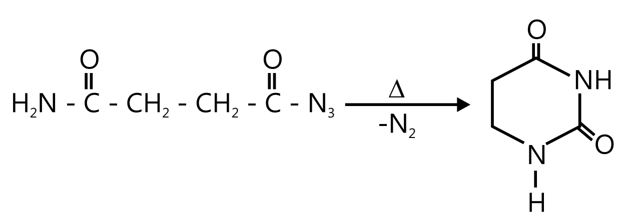


Sol 3: (B)

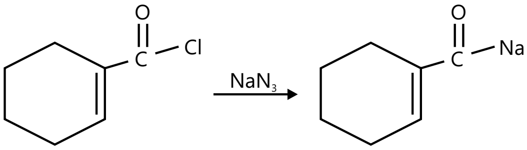
$$HOOC-CH_2-CH_2-CH=CH_2 \xrightarrow{SOCl_2} ClOC-CH_2-CH_2-CH=CH_2$$



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

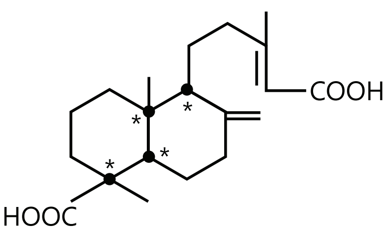
Sol 8: (D) The given compound is optically active.

Comprehension Type

Paragraph 1 (Questions 9 to 12)

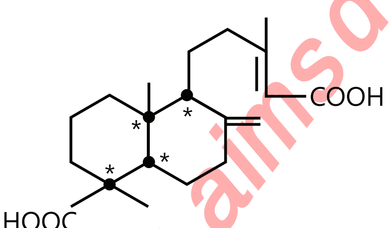
Sol 9: (A) Abstraction of α -H takes place to given a carbanion, from the lower side to give C_2OH_{38}

Sol 10: (C) Agathene Dicarboxylic Acid:



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

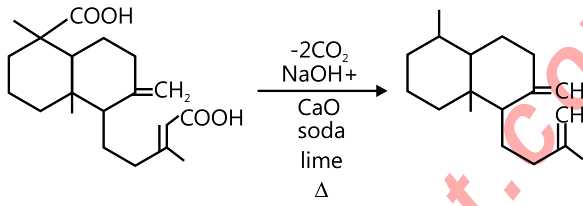
Sol 11: (C) No. of Chiral carbons = 4.



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

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

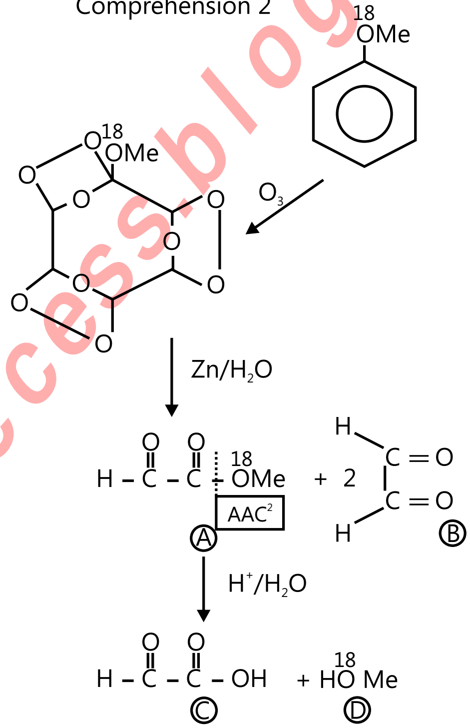
Sol 12: (A)



Paragraph 2 (Questions 13 to 15)

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

Comprehension 2



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

Match the Columns

Sol 19: A $\to$ s; B $\to$ p; C $\to$ r; D $\to$ 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 $A \to p; B \to q, s; C \to r.$

(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 $A \to p; B \to r, t; C \to p, s; D \to p, q, s$

(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 $A \to q, r; B \to p, q; C \to r, s$

(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 $A \to q ; B \to r; C \to p; D \to r; E \to s, t$

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

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

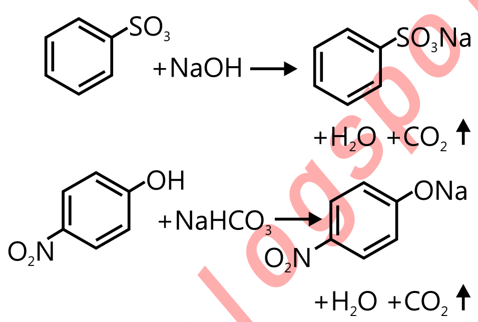
(C) $R' - CH_2 - Br \xrightarrow{LAH} R'CH_3$

(D) $R' - \underset{\underset{O}{\parallel}}{C} - H \xrightarrow{SBH/EtOH} R'CH_2OH$

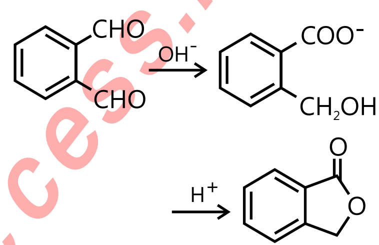
(E) $R - \underset{\underset{O}{\parallel}}{C} - OR' \xrightarrow{Red\ P/HI} RCH_3 + R'H$

Previous Years' Questions

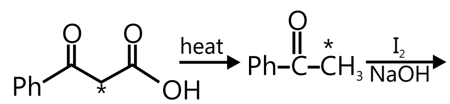
Sol 1: (D)



Sol 2: (C)



Sol 3: (C)



$$\underset{F}{Ph-COONa} + \underset{G}{CHI_3}$$

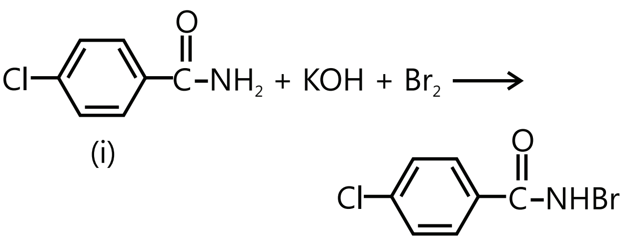
Sol 4; (A, C)

$$R-\overset{\overset{O}{\parallel}}{C}-NH_2 + OH^- + Br_2 \longrightarrow \underset{(A)}{R-\overset{\overset{O}{\parallel}}{C}-NHBr}$$

$$R-\overset{\overset{O}{\parallel}}{C}-NHBr + OH^- \longrightarrow \underset{(B)}{R-\overset{\overset{O}{\parallel}}{C}-\overset{-}{N}-Br}$$

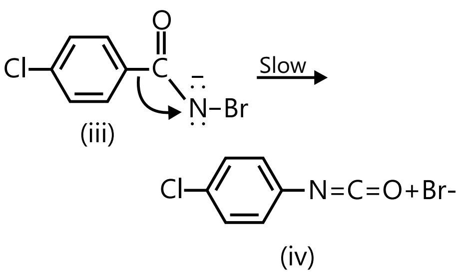
$$\longrightarrow \underset{(C)}{R-N=C=O} + Br^-$$

Sol 5: (D)

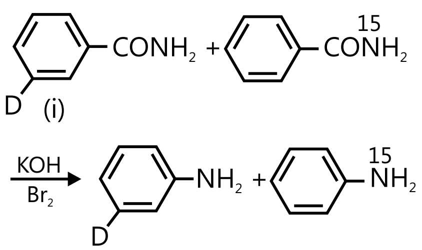


An intermediate (ii)

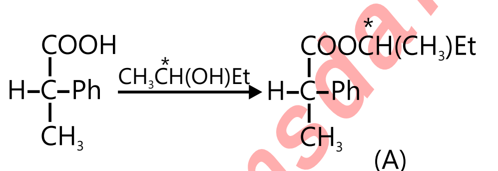
Sol 6: (D)

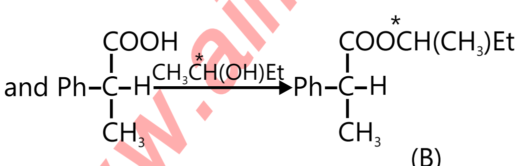


Sol 7: (B) The rate determining step of Hofmann bromide reaction is unimolecular rearrangement of bromamide anion (iii) and no cross-products are formed when mixture of amides are taken.



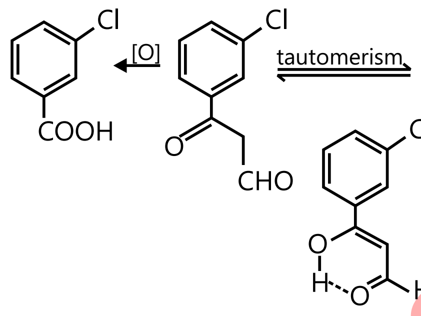
Sol 8: The two stereoisomers of 2-phenyl propanoic acid in the racemic mixture are :



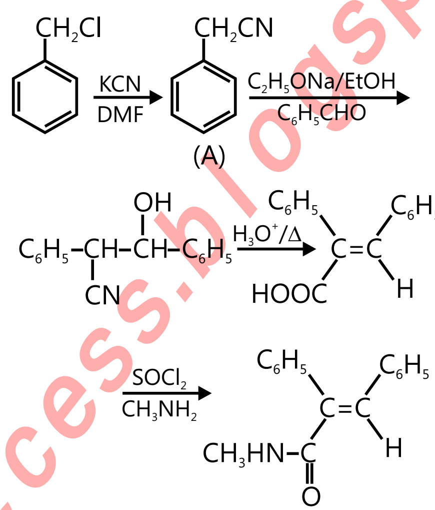


Here A and B are diastereomers.

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 α-H. Enolic forms of B predominates because of presence of intramolecular H-bonding.



Sol 10:



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

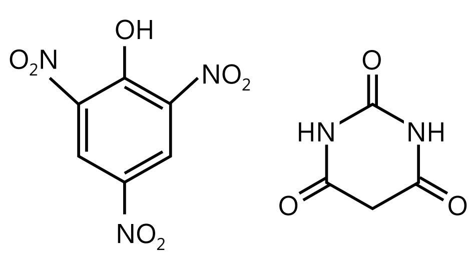
$$CH_3-CH_2-C\equiv C-CH_2-CH_2Br \xrightarrow[3.H_3O^+]{1.Mg/Ether\quad 2.CO_2}$$

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

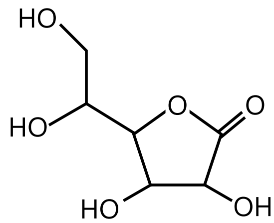
$J = CH_3-CH_2-C\equiv C-CH_2-COOH$

$K = SOCl_2$

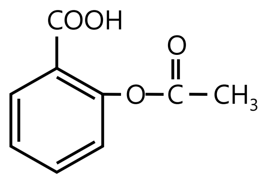
Sol 13: (D)



(Picric Acid) (Barbituric Acid)

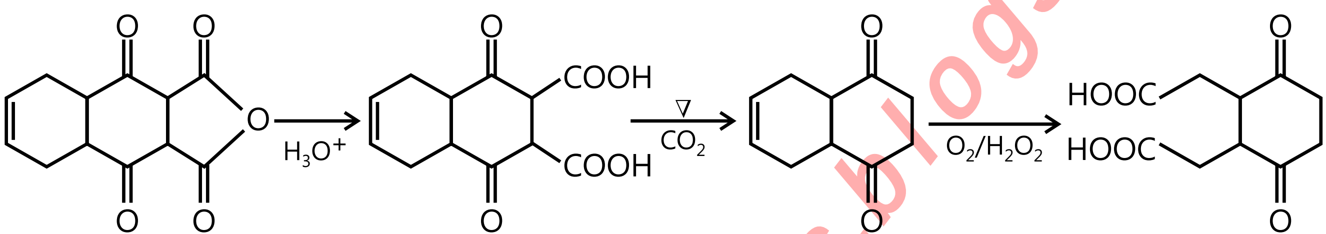


(Ascorbic Acid)

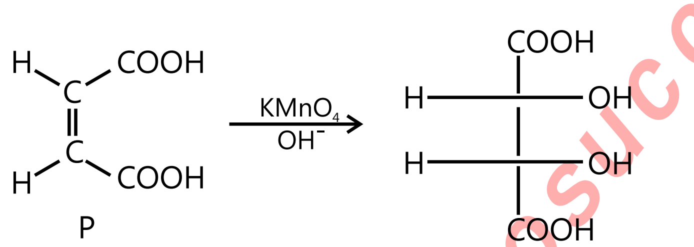


(Asprin)

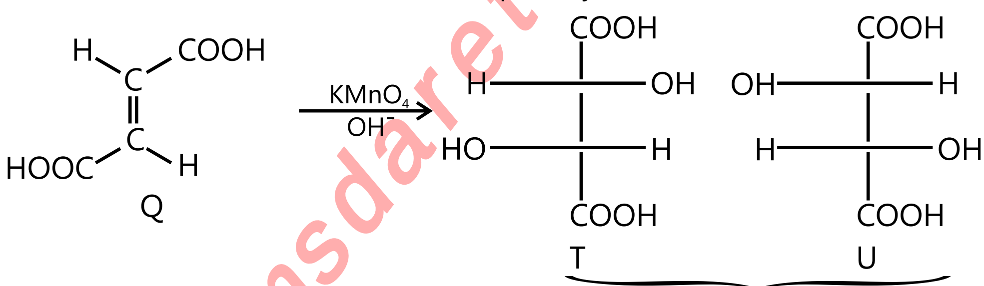
Sol 14: (B)



Sol 15: (B)

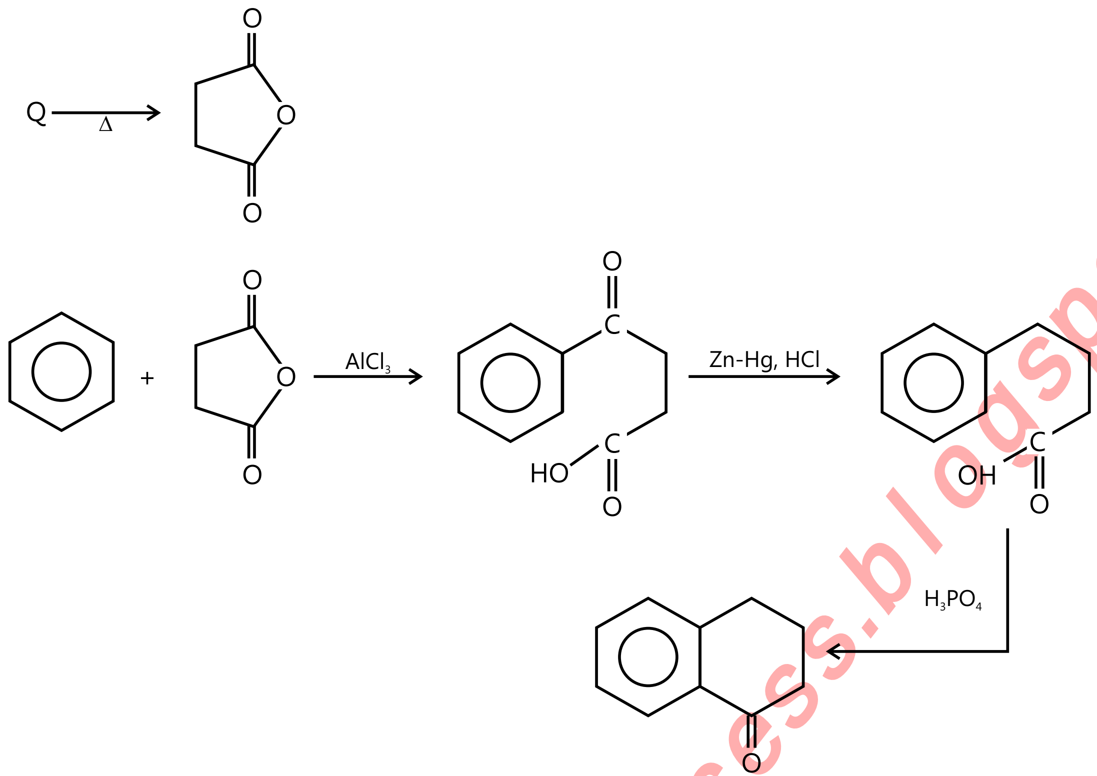


S→optically inactive

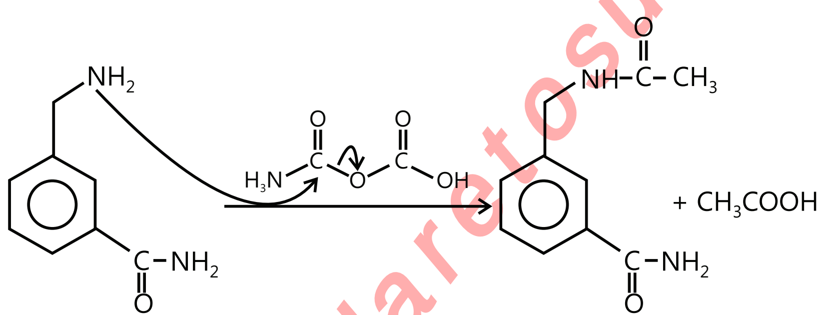


Optically inactive pair

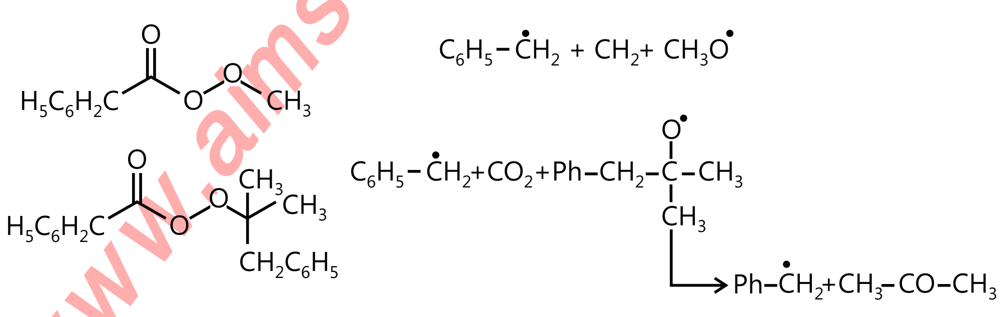
Sol 16: (A)

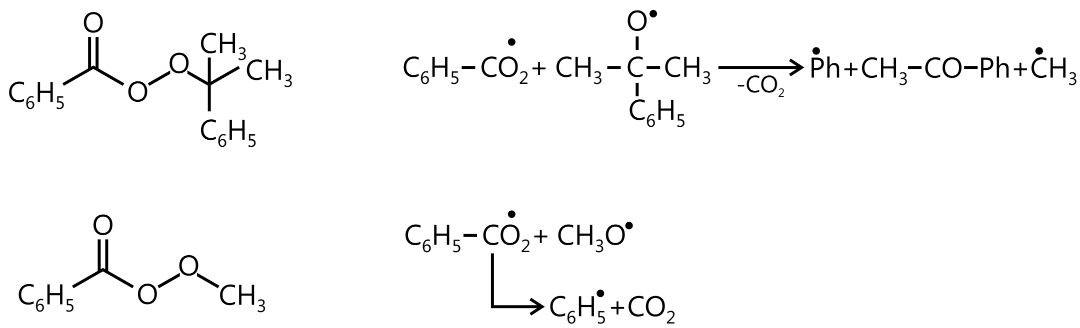


Sol 17: (A) Only amines undergo acetylation and not acid amides.

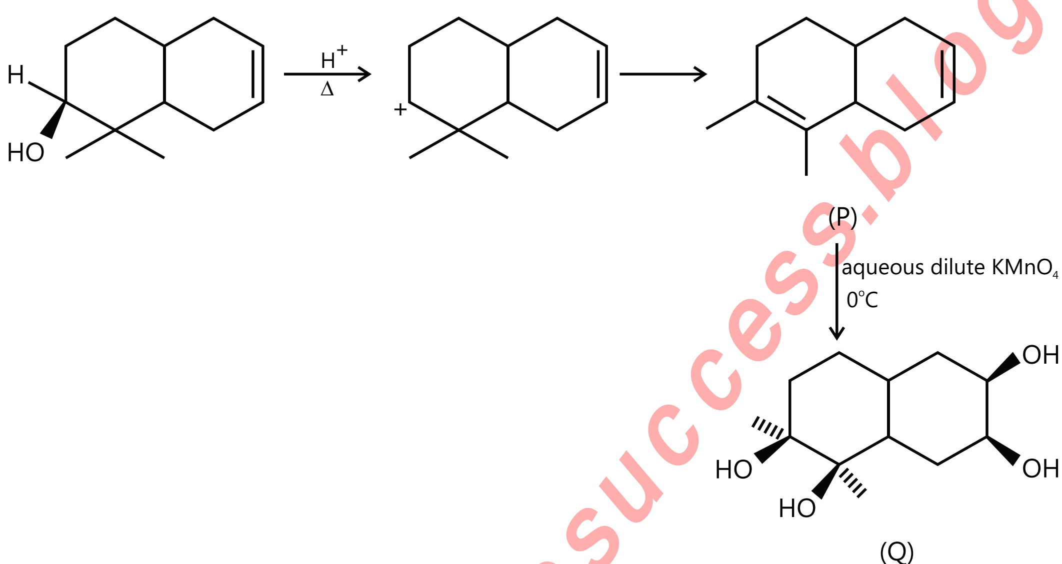


Sol 18: (A) (i) - p; (ii) - r; (iii) - s; (iv) - q

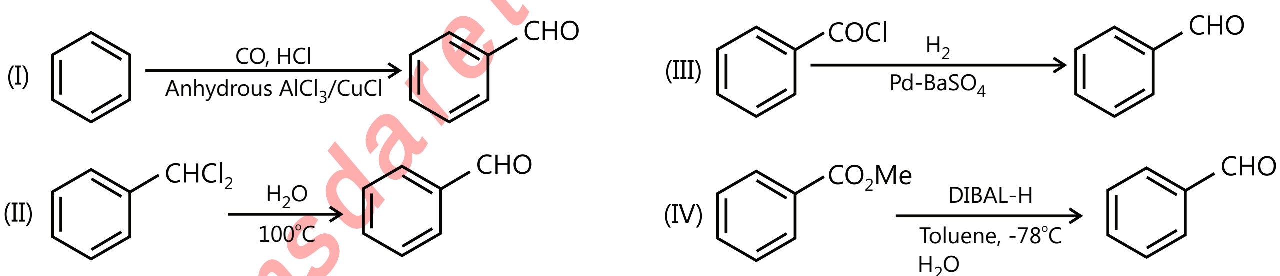




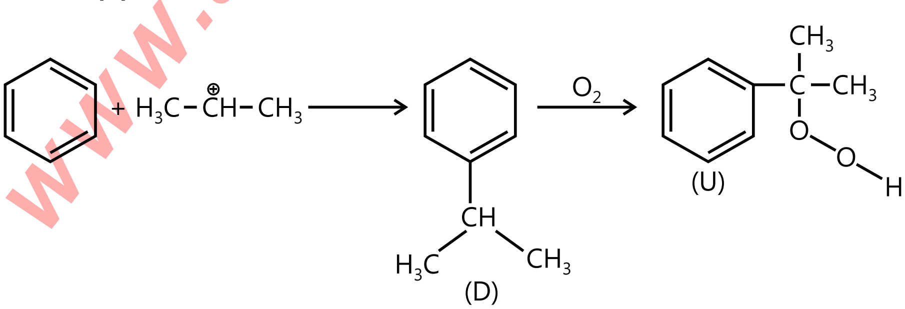
Sol 19: (D)



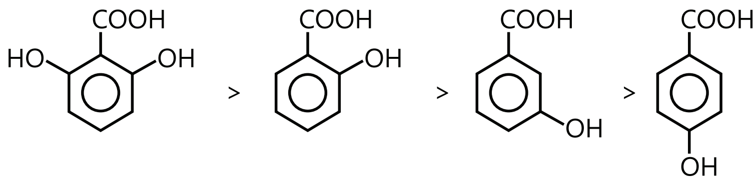
Sol 20: (A, B, C, D)



Sol 21: (B)

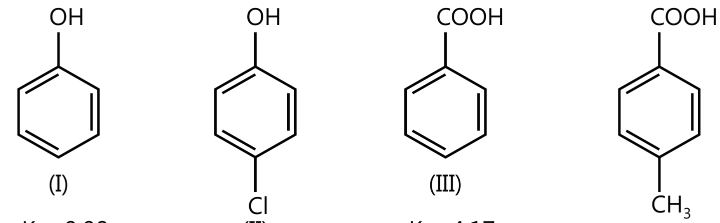


Sol 22: (A)



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

Sol 24: (A)



(I) pKa=9.98

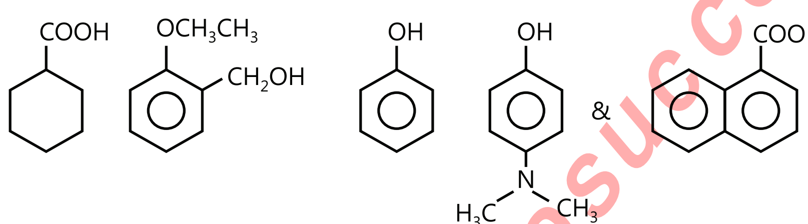
(II) pKa=9.38

(III) pKa=4.17

(IV) pKa=4.37

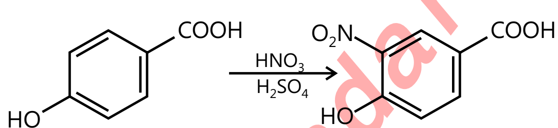
Decreasing order of acidic strength: III > IV > II > I

Sol 25: (5)



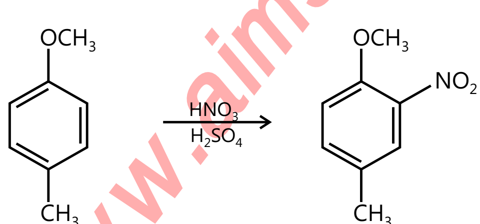
are soluble in aqueous NaOH.

Sol 26: (C)

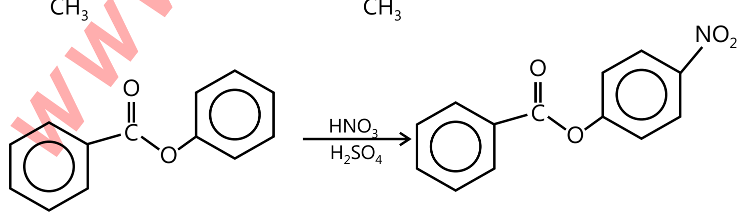


(P)

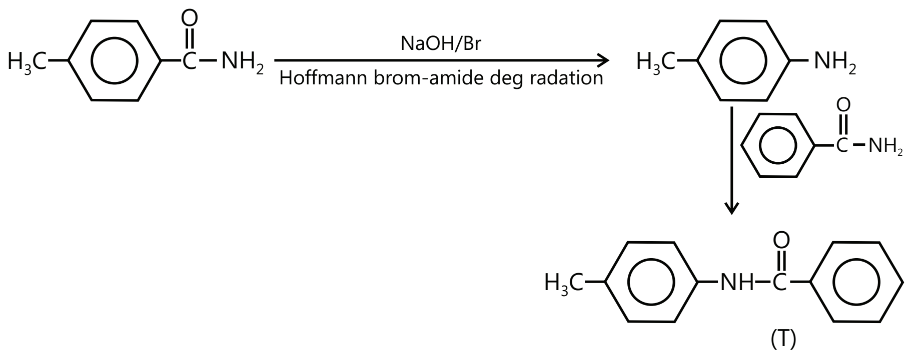
(-OH group is more activating)



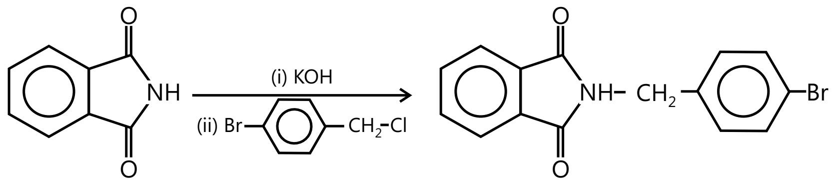
($-OCH_3$ group is more activating)



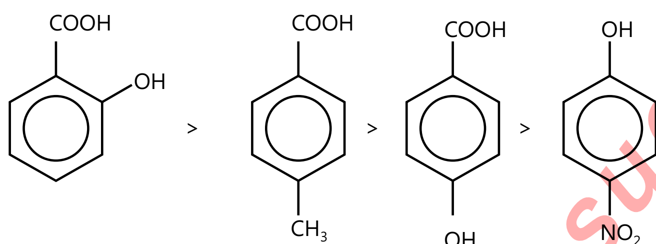
Sol 27: (C)



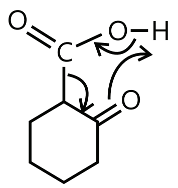
Sol 28: (A)



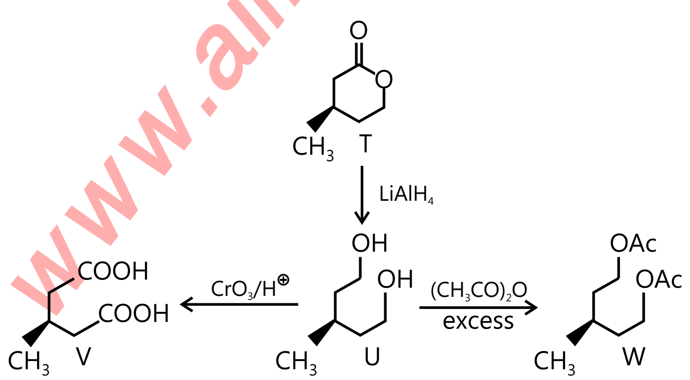
Sol 29: (C) Due to ortho effect o-hydroxy benzoic acid is strongest acid and correct order of decreasing K_a is



Sol 30: (B) In decarboxylation, β-carbon acquire δ^- charge. Whenever δ^- 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)



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