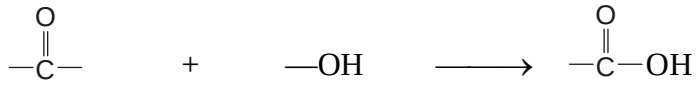
CARBOXYLIC ACID & AMINES

Organic compounds having –COOH group called Carboxylic group.This functional group is composed of Carbonyl ($-\overset{\overset{O}{\|}}{C}-$) and hydroxyl (—OH) group.



Carbonyl group Hydroxyl group Carboxylic group

The properties of the carboxylic group are not simply the combined properties of these two groups, but it has its own distinctive properties.The acidic nature of carboxylic acids is due to the presence of replaceable H-atom in the Carboxylic group.The general formula is $C_nH_{2n}O_2$.

❑ Classification :

Monocarboxylic acid (RCOOH) :

Having one carboxylic group, also called monobasic acid.

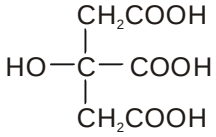
General formula - $C_nH_{2n}O_2$ (n = 1, 2, 3, ...).Higher mono carboxylic acids are called **fatty acids**.

Example : CH_3COOH acetic acid

Dicarboxylic acid : Having two carboxylic groups, also called dibasic acid.

Example :  Oxalic acid

Tricarboxylic acid : Having three carboxylic groups also called tribasic acid.

Example :  Citric acid

NOMENCLATURE

Acid	Common name	IUPAC name
HCOOH	Formic acid (formica-red ants)	Methanoic acid
CH_3COOH	Acetic acid (acetum-vinegar)	Ethanoic acid
CH_3CH_2COOH	Propionic acid (Propan-first pion-fat)	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid (Butter-butyrums)	Butanoic acid
$CH_3CH_2CH_2CH_2COOH$	Valeric acid (valerian-plant root)	Pentanoic acid
$C_5H_{11}COOH$	Caproic acid	Hexanoic acid
$C_7H_{15}COOH$	Caprylic acid	Octanoic acid
C_9H_{19} COOH	Capric acid	Decanoic acid

Last three acids are found in goat fat word - (Caper-Goat).

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

❑ General Method of Preparation

1. By oxidation of primary alcohol with acidic $KMnO_4$ or acidic $K_2Cr_2O_7$:

$$R–CH_2OH + [O] \xrightarrow[K_2Cr_2O_7 / H^+]{KMnO_4 / H^+} RCHO + H_2O \xrightarrow{[O]} RCOOH$$

2. By oxidation of aldehydes :

Aldehydes on oxidation with usual oxidizing agent gives carboxylic acid with same number of carbon atoms as in the aldehyde.

$$R–CHO + [O] \xrightarrow{\text{Tollen's Reagent}} R–COO^- \xrightarrow{H^\oplus} R–COOH$$

$$C_6H_5CHO + [O] \xrightarrow{\text{Tollen's Reagent}} C_6H_5COO^\ominus \xrightarrow{H^\oplus} C_6H_5COOH$$

3. By oxidation of alkenes :

(a) $RCH = CHR' \xrightarrow[(ii)\ H_3O^\oplus]{(i)\ \text{conc. } KMnO_4 / OH^\ominus \text{ heat}} RCOOH + R'COOH$

(b) $RCH = CHR' \xrightarrow[(ii)\ H_2O, \text{Distill}]{(i)\ O_3} RCOOH + R'COOH$

4. By Carboxylation of Grignard Reagent :

$$R–Br \xrightarrow[\text{Dry ether}]{Mg} RMgBr \xrightarrow{CO_2} R–\overset{O}{\overset{\|}{C}}–O^\ominus MgBr^\oplus \xrightarrow[-MgBr(OH)]{H_2O / H^+} R–\overset{O}{\overset{\|}{C}}–OH$$

5. By hydrolysis of acyl derivatives of carboxylic acid :

$$R–\overset{O}{\overset{\|}{C}}–Cl + H_2O \xrightarrow{H^\oplus} R–COOH + HCl$$

$$(R – CO)_2O + H_2O \xrightarrow{H^\oplus} R–COOH + R–\overset{O}{\overset{\|}{C}}–OH$$

$$R – COOR' + H_2O \xrightarrow{H^\oplus} R–COOH + ROH$$

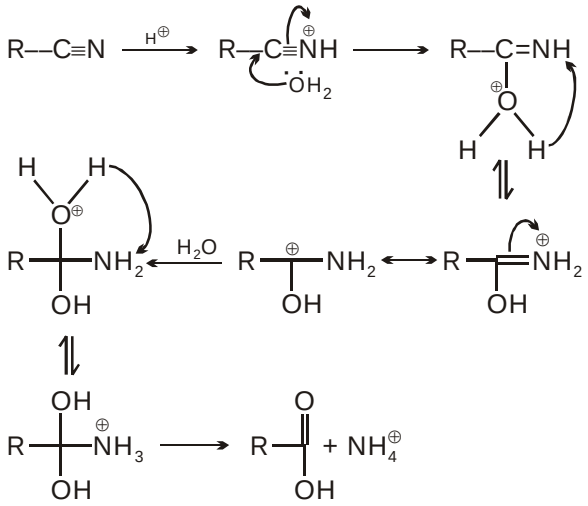
$$R–\overset{O}{\overset{\|}{C}}–NH_2 + H_2O \xrightarrow{H^\oplus} R–COOH + NH_4^\oplus$$

6 Cyanide hydrolysis with dilute acids :

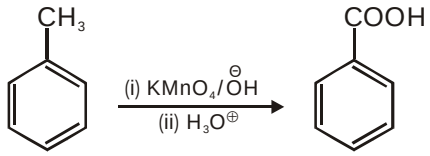
$$R – CN \xrightarrow{H_3O^\oplus} RCOOH$$

The mechanism of hydrolysis of R–CN is as follows.

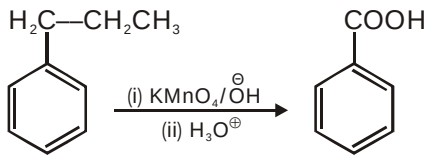
node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & it's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

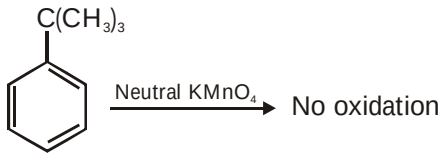


7. By oxidation of alkyl benzene :



Alkyl group having no α-H atom will not be oxidized to –COOH. Any alkyl group containing at least one α-H atom will be oxidized to –COOH. The product of oxidation will be benzoic acid.





The order of benzoic acid formation by oxidation of alkyl benzene.

Methyl benzene >1° alkyl benzene >2° alkyl benzene

1. Describe the preparation of acetic acid from acetylene.

2 Identify Z in the sequence

$$CH_3COONH_4 \xrightarrow[(ii)\,P_2O_5]{(i)\,heat} Y \xrightarrow{H_2O(H^+)} Z$$

(A) $CH_3CH_2CONH_2$ (B) CH_3CN

(C) CH_3COOH (D) $(CH_3CO)_2O$

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

3. A halogen compound 'A' on hydrolysis with dilute alkali followed by acidification gives acetic acid. The compound X is -

(A) $ClCH_2CH_2Cl$ (B) CH_3CHCl_2

(C) $ClCH_2CHCl_2$ (D) CH_3CCl_3

4. Acetic acid is obtained when -

(A) Methyl alcohol is oxidised with potassium permangnate

(B) Formaldehyde is oxidised with potassium dichloromate and sulphuric acid

(C) Acetonitrile is hydrolysed with a dilute mineral acid

(D) Glycerol is heated with sulphuric acid

5. Identify Z in the following reaction sequence $CH_3I \xrightarrow[Ether]{Mg} X \xrightarrow[H^+]{CO_2} Y \xrightarrow[RedP]{Cl_2} Z$

(A) CH_3COOH (B) CH_3MgI (C) CH_3COCl (D) $ClCH_2COOH$

6. Kolbe's electrolysis of aqueous potassium ethanoate leads to the formation of -

(A) Ethene (B) Methane (C) Ethane (D) Ethyne

7 $A \xleftarrow[HI]{red\ P} CH_3COOH \xrightarrow{LiAlH_4} B$. What is not true for A and B -

(A) A is hydrocarbon of general formula C_nH_{2n+2} while B belongs to alkanol

(B) A can be obtained by reducing CH_3CH_2Cl while B by its hydrolysis

(C) A is alkane while B is alkanal

(D) A and B both belongs to different homologous series

8. Arrange the following compounds in decreasing order of acidity -

$ClCH_2CH_2CH_2COOH$ (I) $CH_3CHClCH_2COOH$ (II) $CH_3CH_2CHClCOOH$ (III)

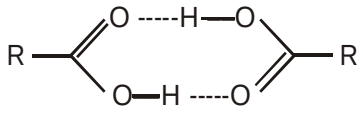
(A) I > II > III (B) III > II > I (C) I > III > II (D) III > I > II

9. Arrange $OHCH_2COOH$ (I), $HOCH_2CH_2COOH$ (II) and CH_3COOH (III) in order of acidity -

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

PHYSICAL PROPERTIES OF CARBOXYLIC ACID :

These are polar substances and can form H-bonds with each other to form dimer structures.



◆ **Boiling Point :** Due to dimeric structure, the effective molecular mass of the acid becomes double of the actual molecular mass. Hence carboxylic acids have higher boiling points than alcohols of comparable molecular masses. Due to hydrogen bonding carboxylic acids show appreciable solubility in water. Its solubility in water is greater than alcohol because H-bonding strength is greater in carboxylic acid than alcohol.

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & it's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

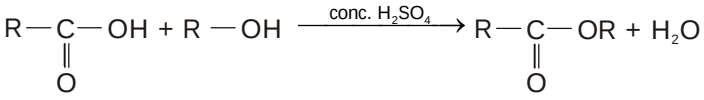
◆ **Melting Point :** Melting point of the carboxylic acid with even number of carbon atoms is higher than acid with odd number of carbon atoms. Such effect is observed in first ten members of the homologous series. This feature is based on the fact that in the carboxylic acids with even number of carbon atoms, the terminal methyl group and carboxylic group are on the opposite sides of zig-zag carbon chain. Hence they fit better in the crystal lattice resulting in stronger inter molecular forces on the other hands acids with odd number of carbon atom have carboxyl and terminal methyl group on the same side of zig-zag carbon chain which result in poor fitting in the crystal lattice. This causes a weak forces among molecules and result for the relatively lower melting point.

The melting point and boiling points are usually higher than those of aliphatic acid of comparable molecular masses. This is due to planar structure of benzene ring in the acid which can pack closely in the crystal than aliphatic acids.

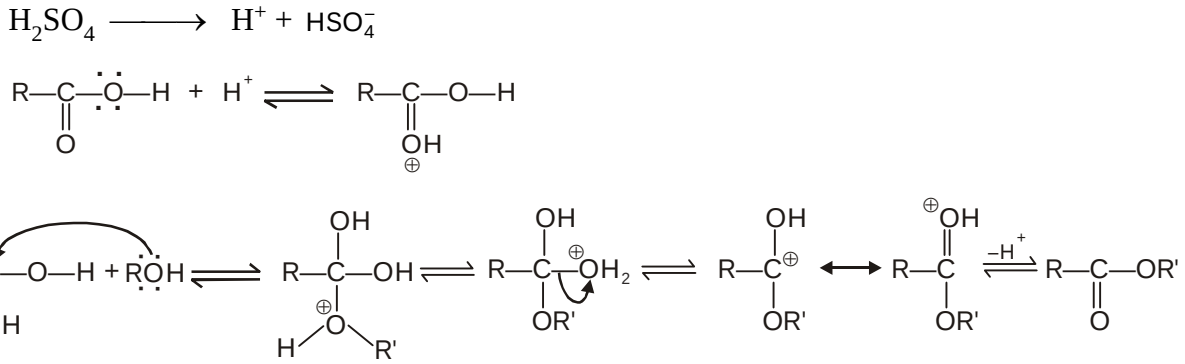
❑ **Reaction Involving Cleavage of –OH Group :**

1. Esterification :

When carboxylic acid reacts with alcohol in the presence of conc. H_2SO_4 to form ester, it is known as esterification



Mechanism :

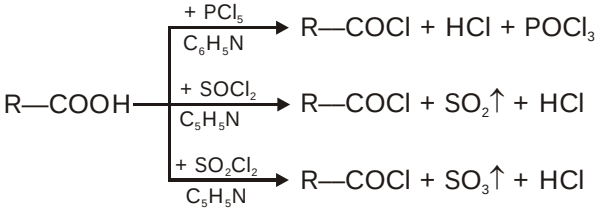


The relative reactivity of alcohol to ester formation markedly dependent on their structure. The greater the bulk of the substituents near the –OH group, the slower the reaction would be same facts is followed by acid as well

$CH_3OH > CH_3CH_2OH > (CH_3)_2 CHOH > (CH_3)_3 COH$

$H—COOH > CH_3COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$

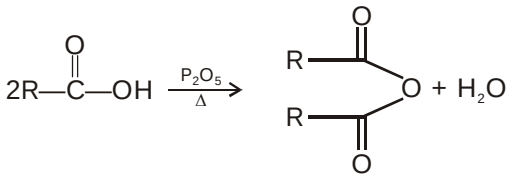
2. Formation of acid chloride :

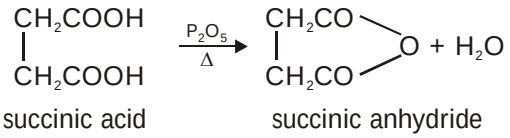


node06\B0B0-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

3. Formation of Acid Anhydride :

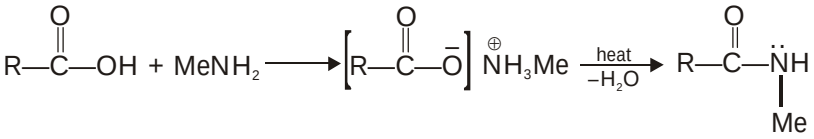
Carboxylic acid on treatment with any dehydrating agent as P_2O_5 to form anhydride by elimination of water molecule.



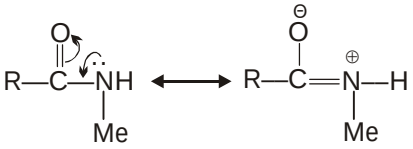


succinic acid succinic anhydride

4. Formation of Amides :



The lone pair electron on N atom undergoes resonance and hence N atom carries partial +ve charge on it.

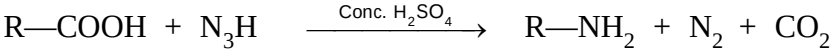


Thus extent of H-bonding increases which makes the boiling and melting points of amides higher than other acid derivatives.

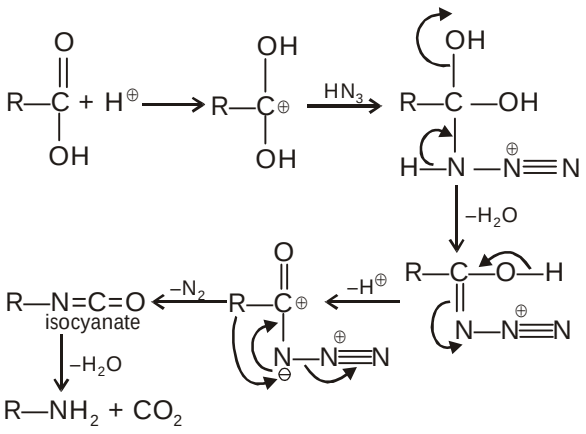
❑ **Reactions Involving –COOH Group :**

1. Schmidt Reaction :

Carboxylic acid reacts with hydrazoic acid in the presence of conc. H_2SO_4 at 90°C forming primary amine.



Mechanism :



node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

2. Soda lime Decarboxylation :

Carboxylic acid on heating with soda lime (NaOH and CaO) give alkane with one carbon atom less than the parent acid.

$$R\text{—}COOH \xrightarrow[\Delta]{\text{sada lime}} R\text{—}H + CO_2$$

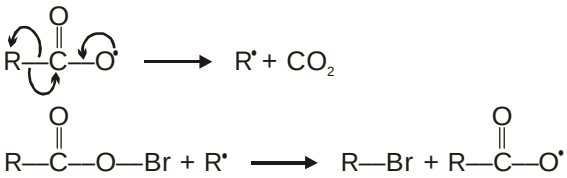
3. Hunsdicker Reaction :

$$R\text{—}COOH \xrightarrow{Ag_2O} R\text{—}COO^- Ag^+ \xrightarrow[\text{in } CCl_4]{Br_2} R\text{—}Br + AgBr + CO_2$$

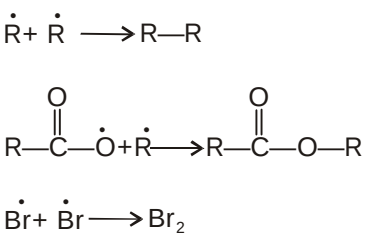
Mechanism : Reaction proceeds through free radical mechanism in various steps.

(i) Chain initiation :

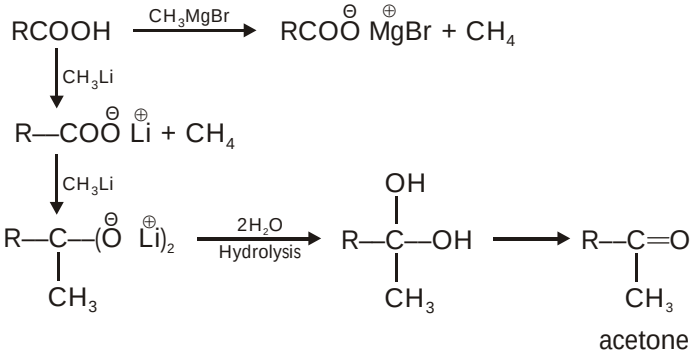
(ii) Chain propagation step :



(iii) Chain termination :



4. With excess of organometallic compounds :

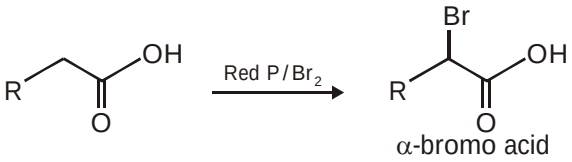


2 moles of organometallic compounds are needed to form ketone.

node06\B0B0-BA\Kota\JEE (Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

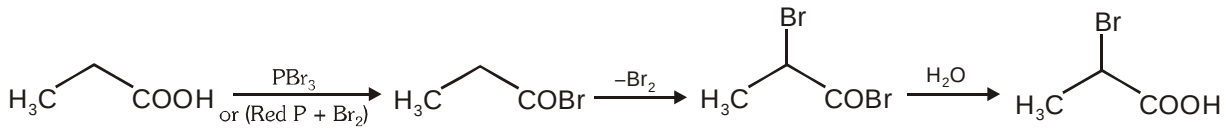
5. Hell-Volhard-Zelinsky Reaction :

This is α-halogenation of a carboxylic acid.

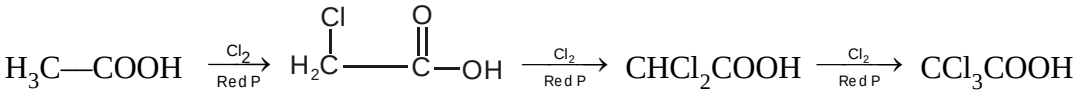


α-bromo acid

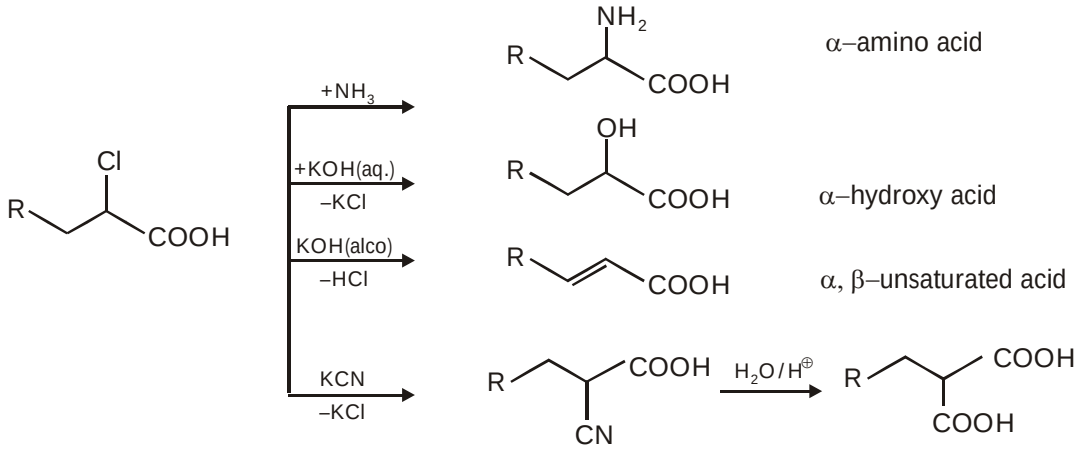
Possible Mechanism for the reaction is :



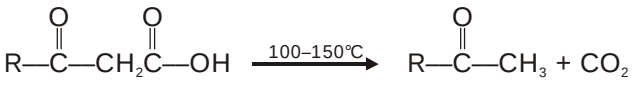
The purpose of PBr_3 is to convert –OH into –Br to make α-hydrogen atom more acidic to be replaced by Br atom of Br_2. The reaction does not stop at monosubstitution but continues till the α-hydrogen are replaced.



The reaction has a great synthetic importance as the halogen atom can be replaced by a number of other groups giving useful products.



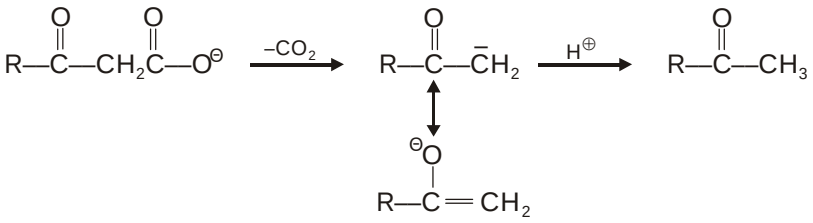
6. Heating of b-keto acid :



β-keto acid

There are two facts on which ease of decarboxylation depends.

(i) When the carboxylate ion decarboxylate, it forms a resonance stabilized enolate anion.

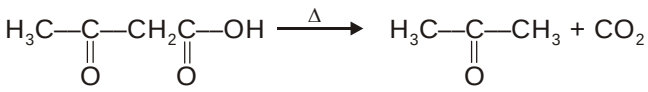


Resonance stabilized enolate anion

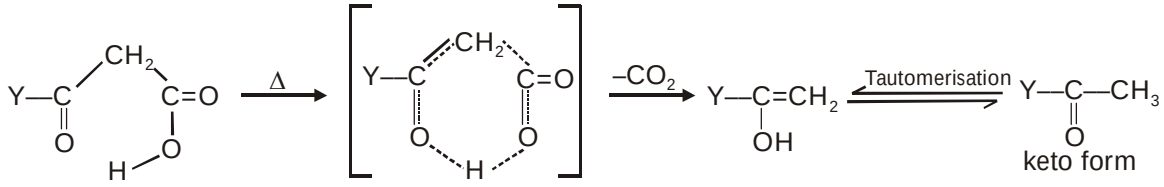
This anion is much more stable than the anion $R\bar{C}H_2$ formed by decarboxylation of an ordinary carboxylic acid anion.

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & it's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

(ii) When the acid itself decarboxylates it can do so through a six-membered cyclic transition state b-keto acid on warming alone or in presence of a base undergoes rapid removal of CO_2.



Mechanism :

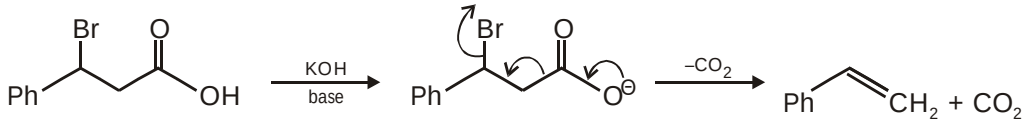


6 membered transition state

Here y can be substituents like

OH – diacid ; R – b-keto acid

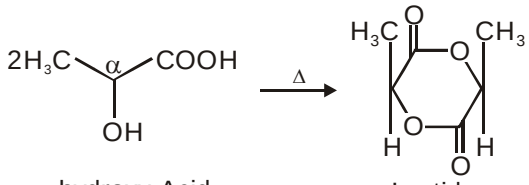
H – b aldehyde acid ; X – b halo acid



This decarboxylation proceeds through elimination.

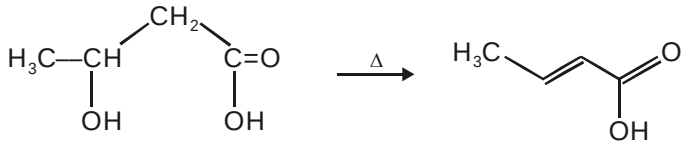
7. Heating of a, b and g Hydroxy Acid :

(i)



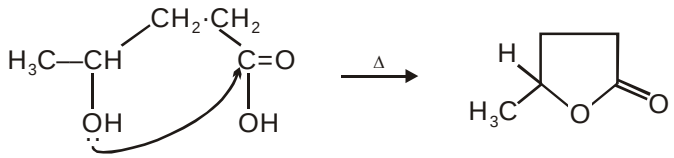
α-hydroxy Acid Lactides

(ii)



β-hydroxy Acid α, β–Unsaturatd Carboxylic Acid

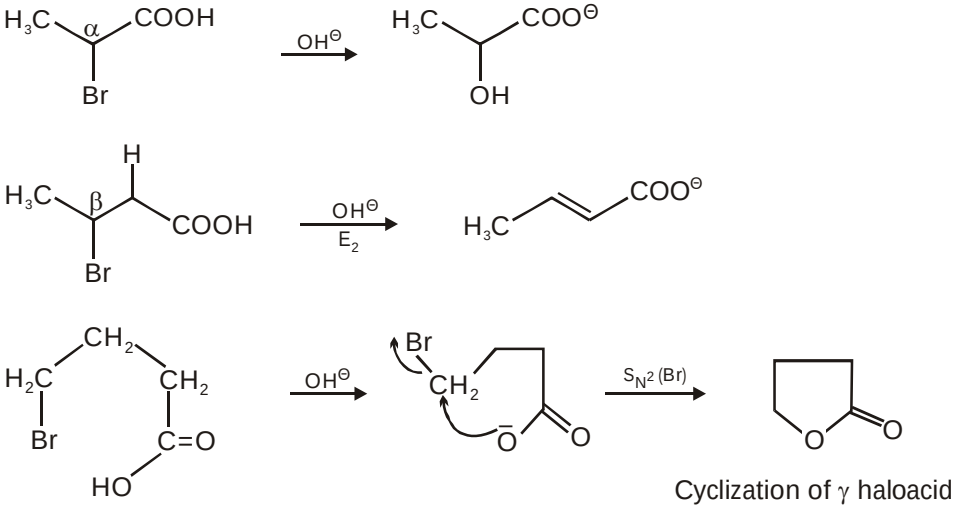
(iii)



γ-hydroxy Acid 5-methyldihydrofuran-2-one

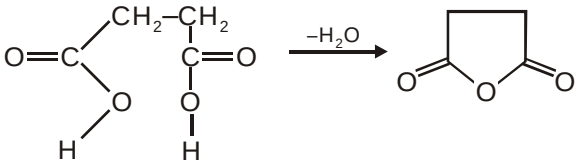
node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

8. Reaction of α, β and γ halo carboxylic acid with aq. NaOH :

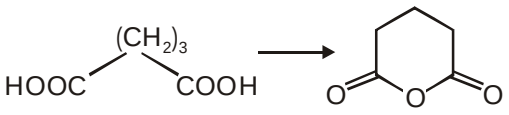


Cyclization of γ haloacid

9. Heating of Dicarboxylic Acids :



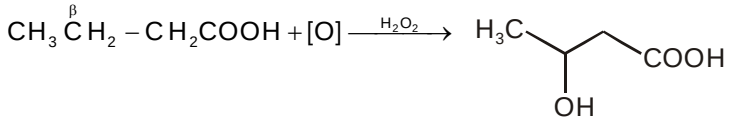
Succinic acid Succinic anhydride



Glutamic anhydride

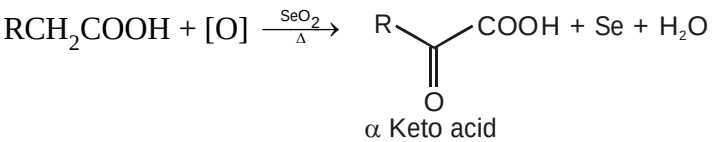
10. Oxidation of Carboxylic acid at Alkyl Group :

Acid on treatment with mild oxidising agent such as H_2O_2, is oxidized at the β position.



3-hydroxybutanoic acid

Oxidation can also occur at α carbon atom on treatment with oxidizing agent like selenium dioxide SeO_2.



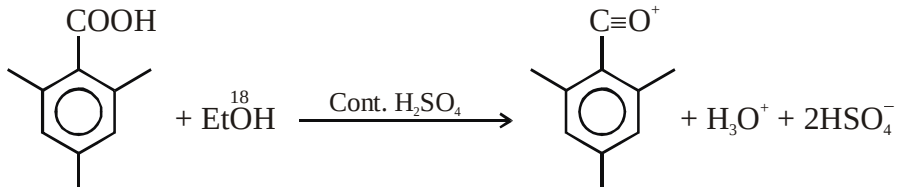
α Keto acid

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & it's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

10. $CH_3-\underset{\underset{O}{\|}}{C}-OH + EtOH \xrightarrow{H^+} CH_3-\underset{\underset{O}{\|}}{C}-O-Et$

11. $CH_3-\underset{\underset{O}{\|}}{C}-OH + Ph_3COH \xrightarrow{H^+} CH_3-\underset{\underset{O}{\|}}{C}-O-CPh_3$

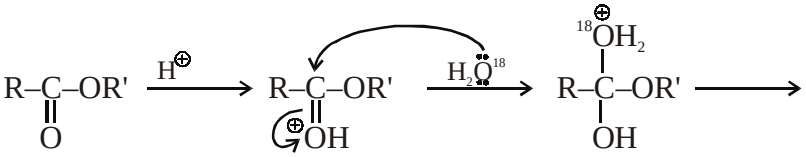
12. $Ph-COOH + PhOH \xrightarrow{H^+} Ph-\underset{\underset{O}{\|}}{C}-O-Ph + H_2O$

13. 

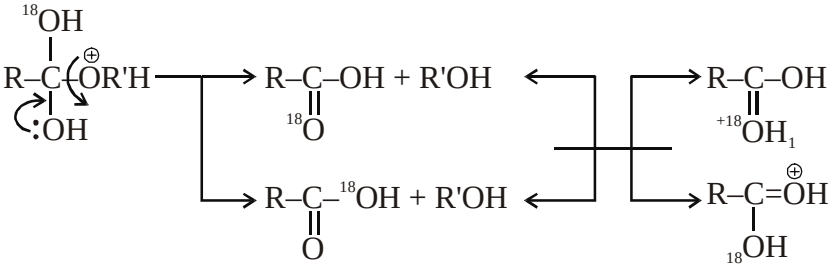
14. $R-\underset{\underset{O}{\|}}{C}-O-R' \xrightarrow[H^+]{H_2O^{18}}$

Traces of O^{18} is founed in ester.

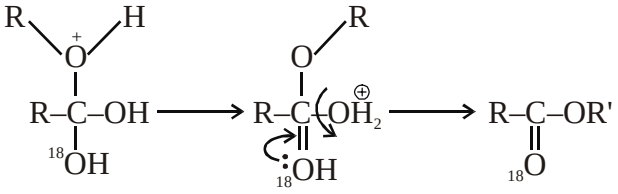
Mechanism :

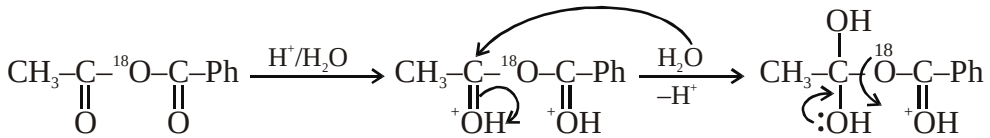


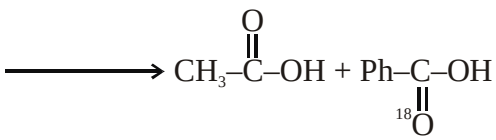
(i)



(ii)

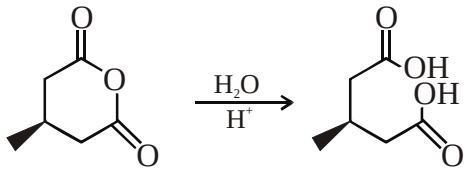




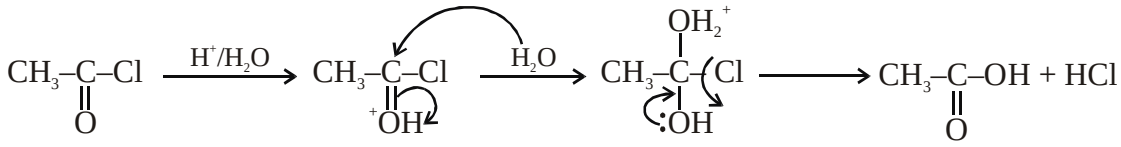


node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

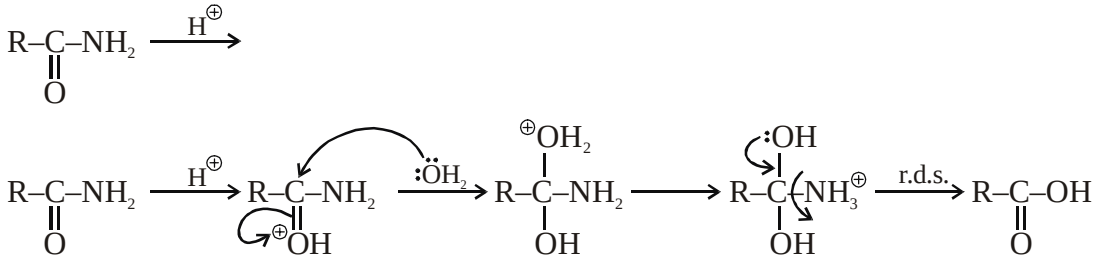
15.



16.

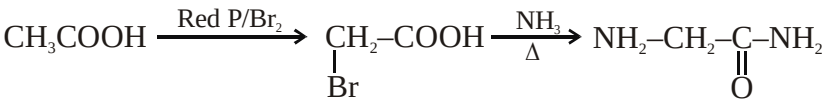


17.



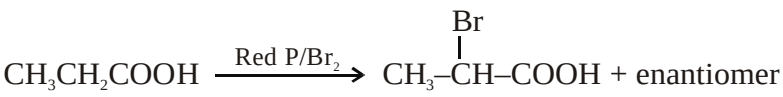
Ex.1 $CH_3COOH \xrightarrow{\text{Red P/Br}_2} P \xrightarrow{NH_3} Q$

Sol.

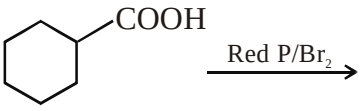


Ex.2 $CH_3CH_2COOH \xrightarrow{\text{Red P/Br}_2} P + Q$

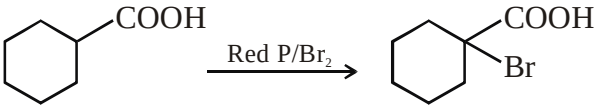
Sol.



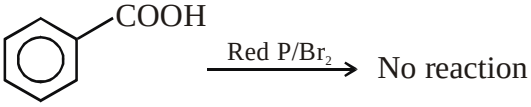
Ex.3



Sol.

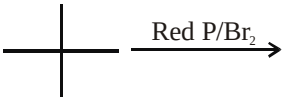


Ex.4

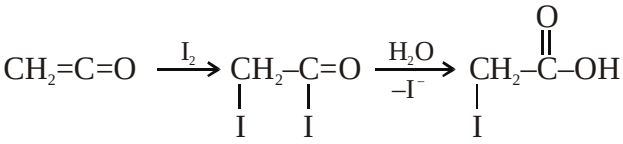


Ex.5 $HCOOH \xrightarrow{\text{Red P/Br}_2}$ No reaction

Ex.6



Ex.7 $CH_2=C=O \xrightarrow{I_2} P \xrightarrow{H_2O} Q$



node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & it's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

Ex.8 $CH_3COOH \xrightarrow[(ii)\ Br_2]{(i)\ Red\ P/Cl_2/cat} CH_2(Br)–COOH$

Ex.9 $CH_3–COOH \xrightarrow[(ii)\ Cl_2]{(i)\ red\ P/Br_2(cat.)} CH_2(Cl)–COOH$

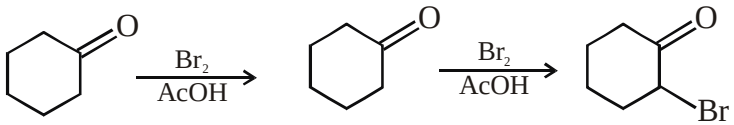
Ex.10. $CH_3–\underset{\underset{O}{\|}}{C}–Cl \xrightarrow{Br_2}$

$CH_3–\underset{\underset{O}{\|}}{C}–Cl \overset{tauto}{\rightleftharpoons} CH_2=\underset{\underset{:OH}{|}}{C}–Cl \xrightarrow[-HBr]{Br–Br} CH_2Br–\underset{\underset{O}{\|}}{C}–Cl$

Ex.11. $CH_3–\underset{\underset{O}{\|}}{C}–OR' \xrightarrow{Br_2}$

$CH_3–\underset{\underset{O}{\|}}{C}–OR' \overset{tauto}{\rightleftharpoons} CH_2=\underset{\underset{:OH}{|}}{C}–OR' \xrightarrow[-HBr]{Br–Br} CH_2(Br)–\underset{\underset{O}{\|}}{C}–OR'$

Ex.12. $CH_3–\underset{\underset{O}{\|}}{C}–CH_3 \xrightarrow[AcOH]{Br_2} CH_3–\underset{\underset{O}{\|}}{C}–CH_2Br$

Ex.13. 

ARNDT-EISTERT SYNTHESIS (AES)

In this reaction, next homologus of carboxylic acid is obtained as product.

$CH_3–\underset{\underset{O}{\|}}{C}–OH \xrightarrow[(ii)\ CH_2N_2\ (iii)\ Ag_2O\ (iv)\ H_2O]{(i)\ SOCl_2} CH_3–CH_2–COOH$

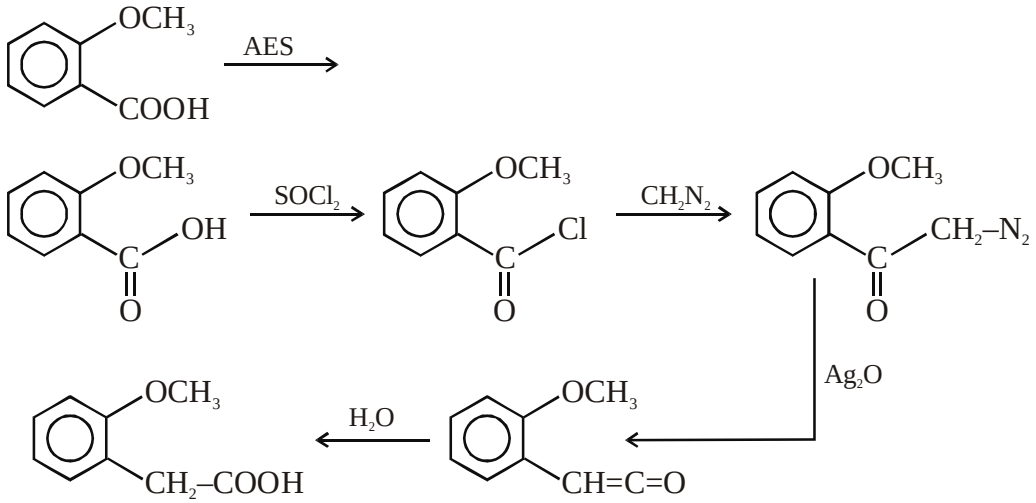
Mechanism :

$CH_3–\underset{\underset{O}{\|}}{C}–OH \xrightarrow{SOCl_2} CH_3–\underset{\underset{O}{\|}}{C}–Cl \xrightarrow{\overset{\ominus}{C}H_2\overset{\oplus}{N}_2} CH_3–\underset{\underset{O}{\|}}{C}–\overset{\ominus}{C}H–\overset{\oplus}{N}_2 \xrightarrow{Ag_2O}$

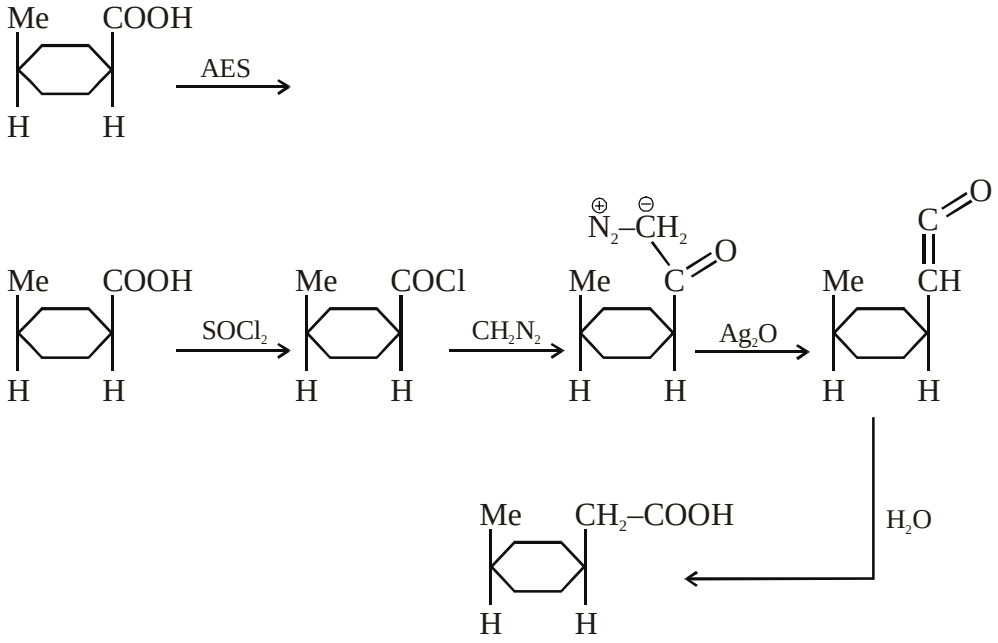
$CH_3–CH=C=O \xrightarrow{H_2O} CH_3–CH_2–\underset{\underset{O}{\|}}{C}–OH$

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

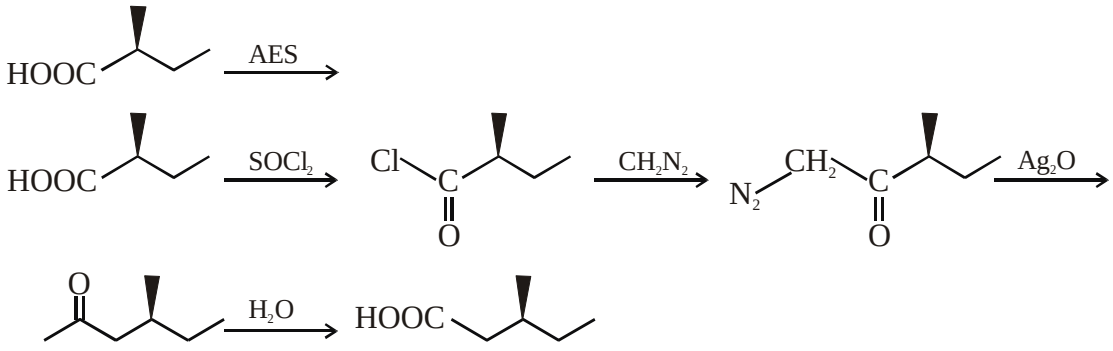
1.



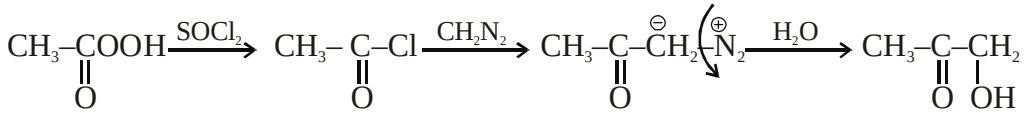
2.



3.

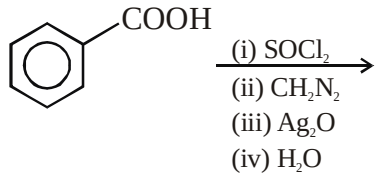


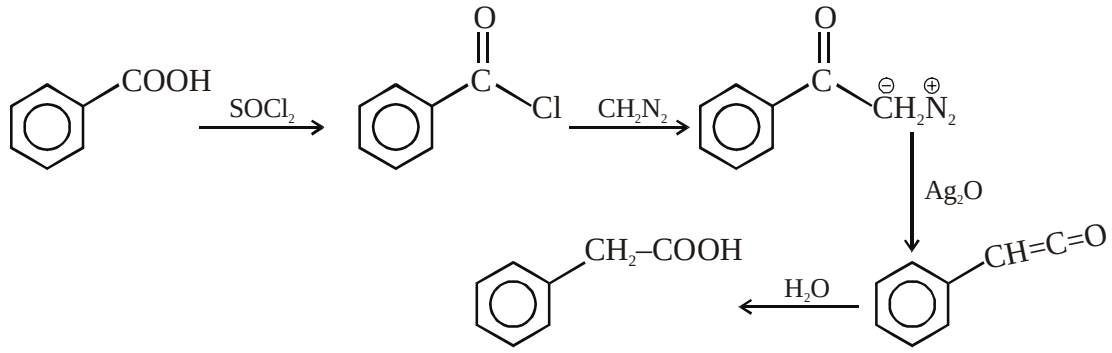
4. $CH_3–COOH \xrightarrow[(iii)\ H_2O]{(i)\ SOCl_2,\ (ii)\ CH_2N_2}$



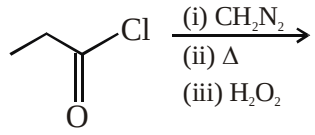
node06\B0080-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & it's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

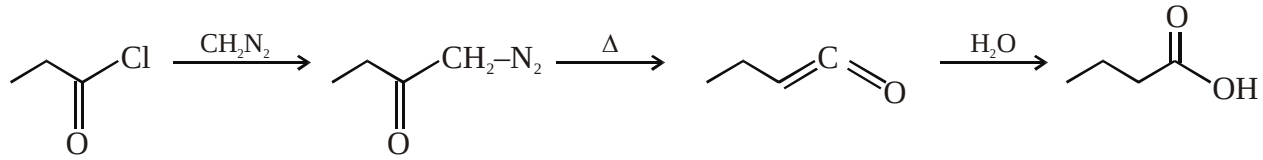
5.





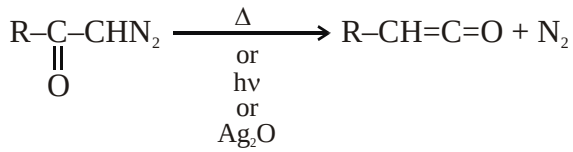
6.



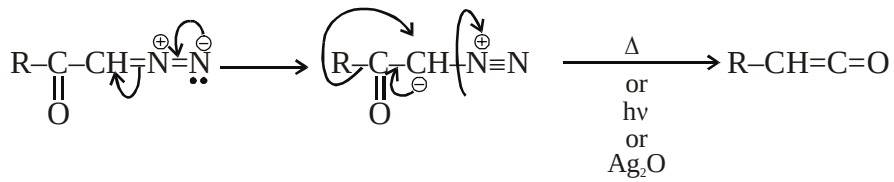


WOLF REARRANGEMENT

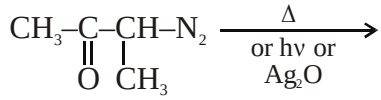
In this reaction, a-diazocarbonyl compound is treated with thermally,photochemically or catalytically so that ketene is obtained.

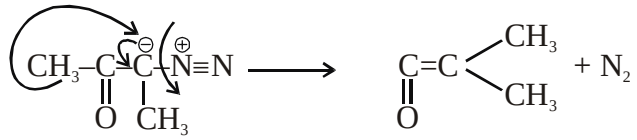


Mechanism :



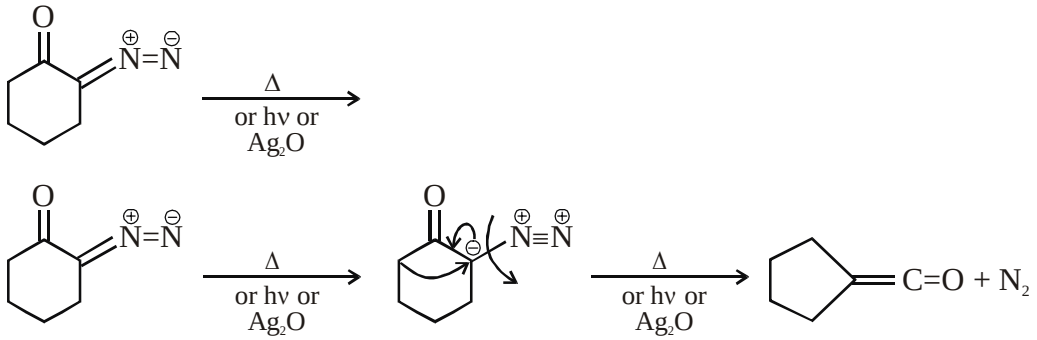
1.



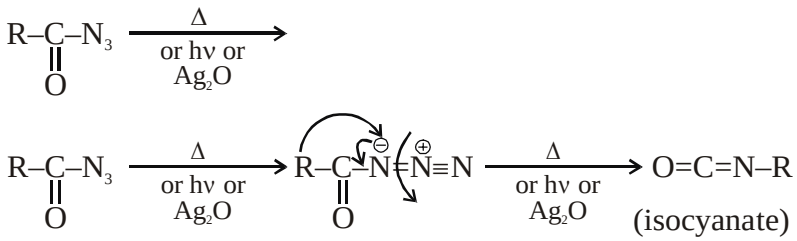


node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

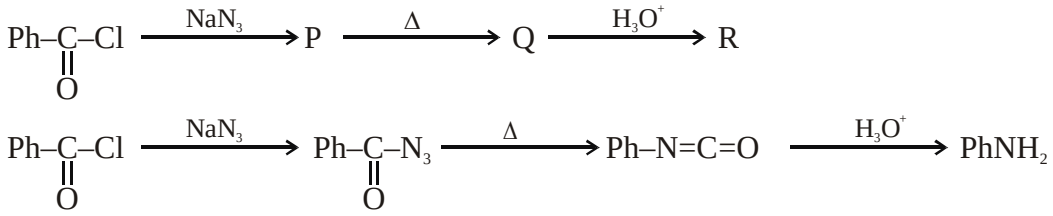
2.



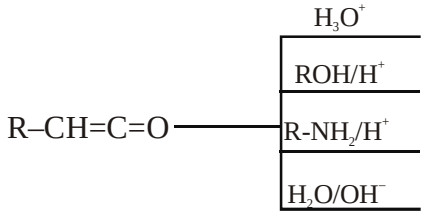
3.



4.



5.



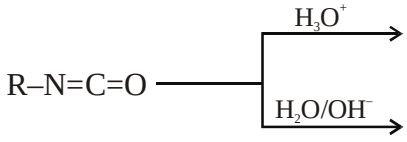
$R–CH=C=O \xrightarrow{H_3O^+} R–CH_2–COOH$

$R–CH=C=O \longrightarrow R–CH_2–COOR$

$R–CH=C=O \xrightarrow{R\text{-}NH_2/H^+} R–CH_2–CONHR$

$R–CH=C=O \xrightarrow{H_2O/OH^\ominus} R–CH_2–COO^\ominus$

6.

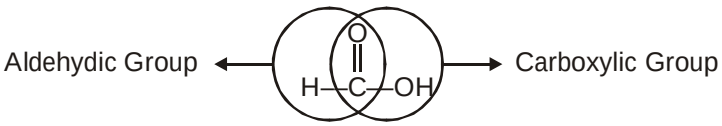


$R–N=C=O \xrightarrow{H_3O^+} R–NH_2$ (decarboxylation takes place during reaction)

$R–N=C=O \xrightarrow{H_2O/OH^\ominus} R–NH_2$

❑ **Abnormal Behaviour of Formic Acid :**

The behaviour of formic acid is different from other carboxylic acid due to presence of aldehydic group.



node06\B0080-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & it's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

❑ **Reaction with :**

(a) **Tollen's reagents** : formic acid behaves as a reducing agent and reduces Tollen's reagent or Felhing solution. But others acid fail to do so.

$H–COOH + Ag_2O \longrightarrow CO_2 + H_2O + 2Ag \downarrow$ Silver mirror

$H–COOH + 2CuO \longrightarrow CO_2 + H_2O + Cu_2O \downarrow$ Red ppt.

(b) **Reaction with $HgCl_2$** : Formic acid forms white ppt. of Hg_2Cl_2 with $HgCl_2$ which is converted to Grey ppt of mercury.

$2HCOOH + HgCl_2 \longrightarrow CO_2 + Hg_2Cl_2 \downarrow + 2HCl$

white ppt.

Test for HCOOH and CH_3COOH

	Test	HCOOH	CH_3COOH
1.	Reducing character		
	Reducing agents -		
	Tollen reagent	Silver mirror	–
	Fehling solution	Cu_2O red	–
	$HgCl_2$	Hg_2Cl_2	–
	Corrosive sublimate	Calomel	–
	$K_2Cr_2O_7$	Cr^{+3}	–
2.	Decarboxylation.	$Na_2CO_3 + H_2$	CH_4
3.	Heating at 160^0C	$CO_2 + H_2$	–
4.	Heating sodium salts of acids at 360^0C	COONa | COONa $\xrightarrow[\Delta]{HCl}$ COOH | COOH + NaCl	–
5.	Conc.H_2SO_4	$CO + H_2O$	Dissolve
6.	P_2O_5	–	Anhydride
7.	Cl_2 / P	$CO_2 + 2HCl$	Products are mono, di, tri chloro acetic acid.
8.	Ca salt heat	HCHO	CH_3COCH_3

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

❑ **Uses of Formic Acid :**

(i) As an antiseptic

(ii) For preservation of fruits.

(iii) For leather tanning.

(iv) In dying wool and cotton fabrics.

(v) As a coagulating agent for rubber.

(vi) For hydrogenation of oil as Ni-formate.

❑ **Uses of Acetic Acid :**

(i) Vinegar (6 - 10% solution) used as **table acid** and manufacture of pickles.

(ii) In the form of salts, it is used in medicine and paints.

(iii) For manufacture of rubber from latex and casein from milk CH_3COOH is used as coagulant.

(iv) Al and Cr acetates are used as mordants.

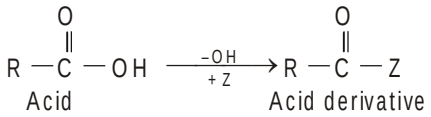
(v) In the manufacture of dyes and perfumes.

(vi) As a solvent and laboratory reagent.

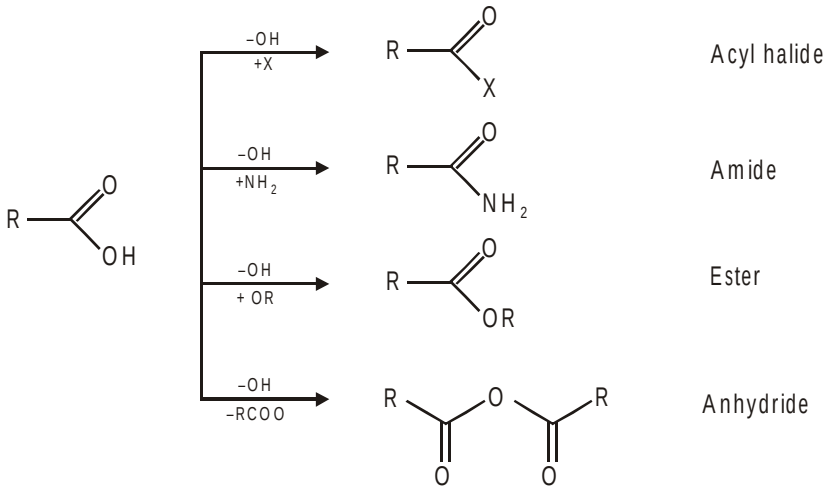
ACID DERIVATIVES

❑ **Derivatives of Carboxylic Acid**

The –OH of an acid can be replaced by –Cl, –OR, or $–NH_2$ group to yield an acid chloride an ester or an amide. These compounds are called functional derivatives of acid and they all contain acyl group. The functional derivatives are all readily converted into the acid by simple hydrolysis.



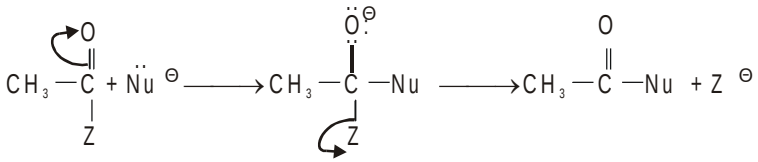
$R—\overset{O}{\overset{\|}{C}}—$ is Acyl group and Z is nucleophile $Cl^{\ominus}$, $CH_3COO^{\ominus}$, $C_2H_5O^{\ominus}$, $NH_2^{\ominus}$ etc.



node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & it's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

Characteristic reaction for acid derivatives is nucleophilic substitution reaction :

Mechanism :



sp^2 hybrid C - atom sp^3 hybrid C - atom

In this reaction Z is leaving group. Weak bases are good leaving groups.

Reactivity order - depends on the basic Character of Z

basicity : $Cl^- < CH_3COO^- < C_2H_5O^- < NH_2^-$

In the given groups Cl^- is the weakest base so it is best leaving group.

Reactivilty order : $CH_3COCl > CH_3COOCOCH_3 > CH_2COOC_2H_5 > CH_3CONH_2$

In acid derivatives the carbonyl group > C═O is attached to highly electronegative Cl^-, CH_3COO, NH_2^- etc. group due to electron withdrawing effect of these groups, the electron density on the carbonyl carbon is reduced further. Thus acetyl group is readily attacked by $\ddot{N}u$ shows nucleophilic substitution reaction.

Basicity of leaving groups :

Weaker the basic character of the leaving group more will be the ease with which the leaving group leaves the compound and hence more is the leaving power

The order of basicity of the leaving group and their leaving tendency follows the order.

$H_2N^- > RO^- > RCOO^- > Cl^-$

Basicity ⟵

Leaving power ⟶

Resonance Effect :

Resonating Structure

Due to resonance, the carbon–leaving group (L) bond acquires a double bond character due to which stabilization occurs. Now more is stabilization, lesser is the reactivity and vice-versa. As the stabilization is the least in the case of acid chloride because of high magnitude of –I effect of Cl atom. Therefore its reactivity is the most.

Nucleophilic acyl substitution should be catalysed by acids becasuse the protonation of the acyl compound would facillitate step (i) for nuceleophilic attack.

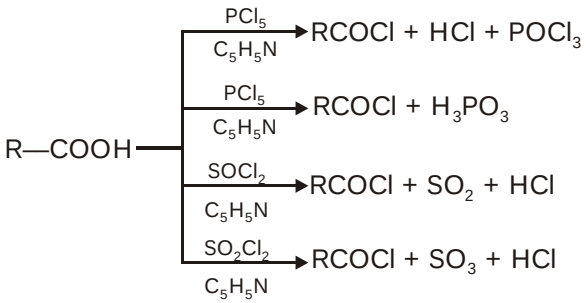
node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

ACYL CHLORIDE (RCOCl)

These are the derivatives of carboxylic acid in which hydroxyl (–OH) part of carboxyl group is replaced by halo group. The most reactive compound of halo leaving group is chloro compounds.

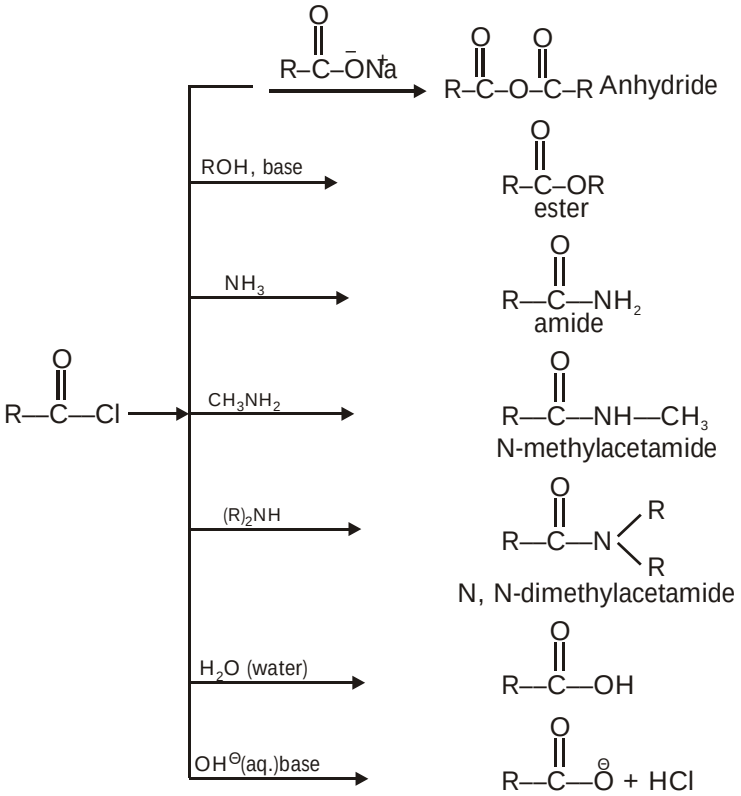
❑ Method of Preparation :

Carboxylic acid chloride can be prepared by the reaction of carboxylic acid with PCl_5 or $SOCl_2$ of PCl_3 or SO_2Cl_2.



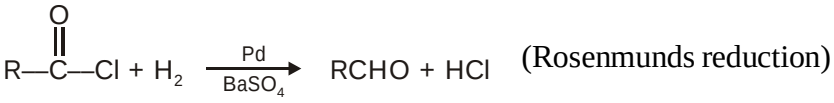
❑ Chemical Properties :

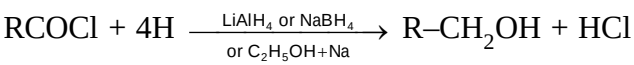
1. Acylation Reaction :



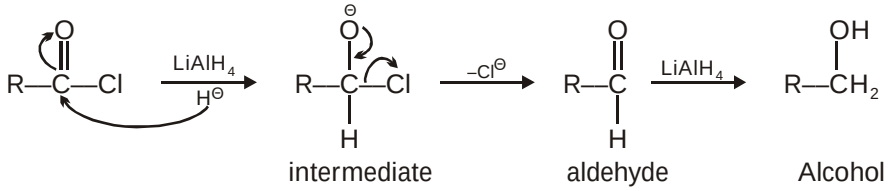
node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & it's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

2. Reduction reactions :

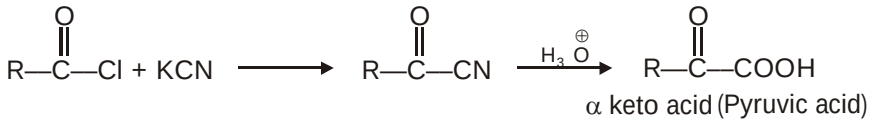




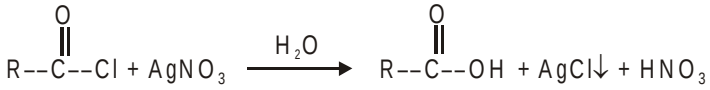
Mechanism :



3. Reaction with KCN :

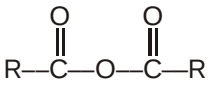


4. Reaction with $AgNO_3$:

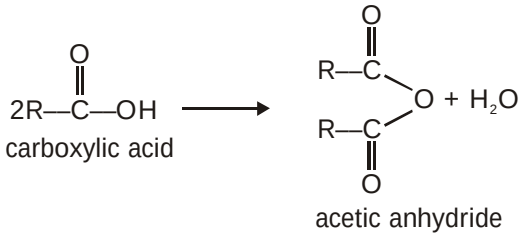


The aliphatic acid chlorides are readily decomposed by water therefore aqueous solution of acid chloride gives white ppt. with aqueous $AgNO_3$.

ACID ANHYDRIDES (RCOOCOR)

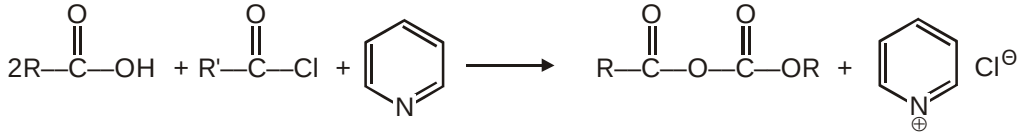


Acid anhydrides are considered to be derived from carboxylic acids by the removal of a molecule of water from two molecules of the acid.



❑ **Method of preparation :**

1. Acylation : Carboxylic acid reacts with acyl chloride in the presence of pyridine to give carboxylic acid anhydride.

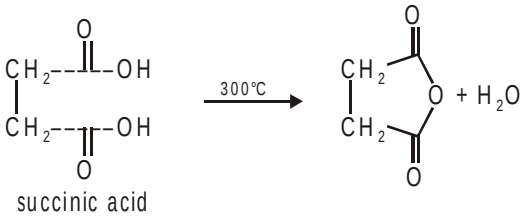


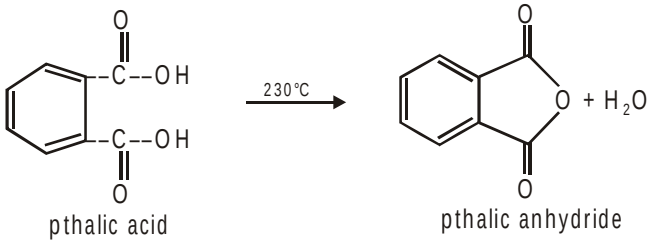
node06\B0B0-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

2. Sodium salt of carboxylic acids also react with acyl chlorides to give :

In this reaction a carboxylate ion acts as a nucleophile and brings about a nueleophilic substitution reaction at the acyl carbon of acyl chloride.

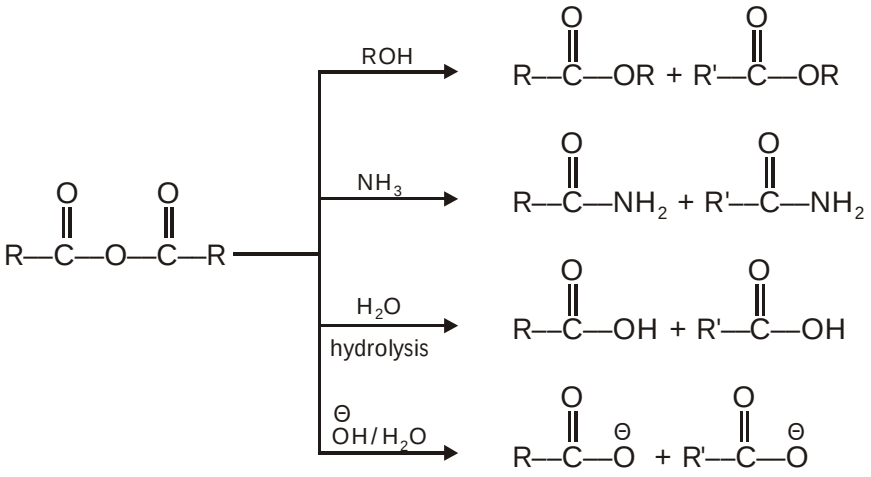
3. Cyclic anhydrides : By simple heating the appropriate dicarboxylic acid. This method leads to a five or six membered ring.





4. Chemical Properties :

Acid anhydride are good acylating agents. Their reactions are less vigorous than the corresponding acyl halides.



node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & it's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

ESTERS (RCOOR)

Ester are the derivative of the carboxylic acid in which the –OH part of the carboxylic group has been replaced by –OR group where R may be alkyl or aryl group.

Method of Preparation :

By reaction of acids wth alcohol or diazomethane in presence of ether.

$$RCOOH + C_2H_5OH \xrightarrow{H^+ / H_2O} R—COOC_2H_5 + H_2O$$

$$R—COOH + CH_2N_2 \xrightarrow{ether} \underset{Ester}{RCOOCH_3} + N_2$$

$$R-\overset{\overset{O}{\|}}{C}-Cl + C_2H_5OH \xrightarrow{C_5H_5N} R-\overset{\overset{O}{\|}}{C}-OC_2H_5 + HCl$$

$$\left(R-\overset{\overset{O}{\|}}{C}-\right)_2 O + C_2H_5OH \xrightarrow{C_5H_5N} R-\overset{\overset{O}{\|}}{C}-OC_2H_5 + R-COOH$$

Chemical Properties :

1. **Conversion to other esters :** Transesterifications

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

2. **Conversion to amides :**

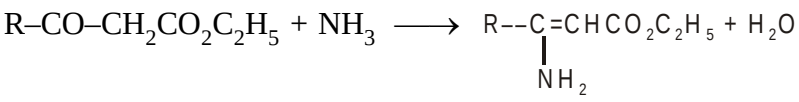
3. **Reaction with Grignard Reagent :**

$$R-\overset{\overset{O}{\|}}{C}-OR + 2R''MgX \xrightarrow{diethylether} R-\underset{\underset{R''}{|}}{\overset{\overset{OMgX}{|}}{C}}-R'' \xrightarrow{H^{\oplus}} \underset{3° \text{ alcohol}}{R-\underset{\underset{R''}{|}}{\overset{\overset{OH}{|}}{C}}-R''} + R'OMgX$$

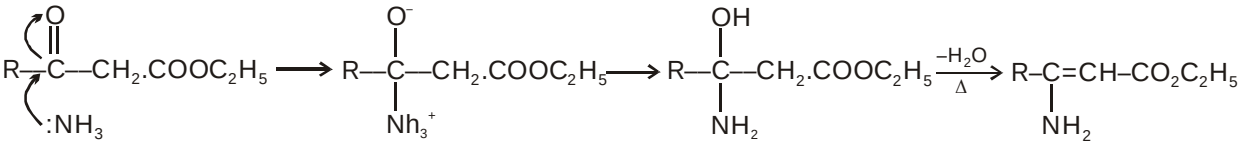
4. **Reduction of ester :**

Phthalic anhydride

5. Reaction of NH_3 with keto ester :

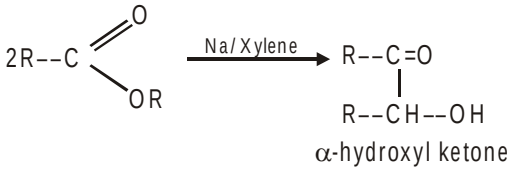


Mechanism :



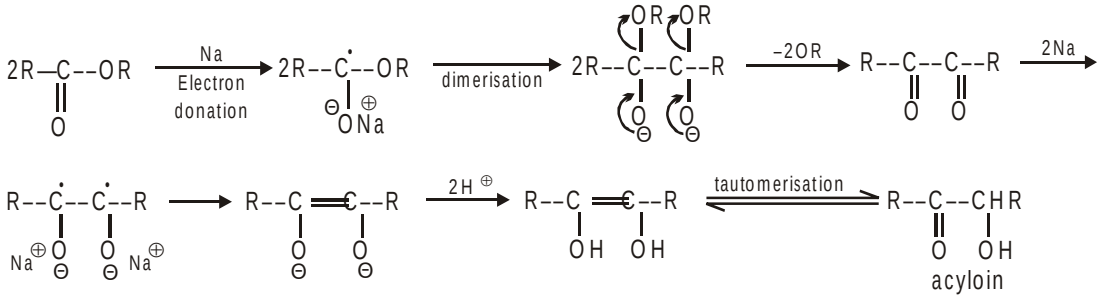
Attack will occur at carbonyl group first because of high degree of +ve charge on carbonyl carbon atom.

6. Acyloin condensation :



Mechanism :

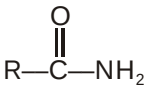
It is the intermolecular, sodium promoted condensation of two moles of ester or the intra molecular condesation of a ester to α-hydroxy ketone (acyloin).



❑ **Hydrolysis of Acyl Derivatives :**

Ester hydrolysis can be carried out in mechanistic pathways $A_{AC^1}, A_{AC^2}, A_{AL^1}, B_{AC^2}$.

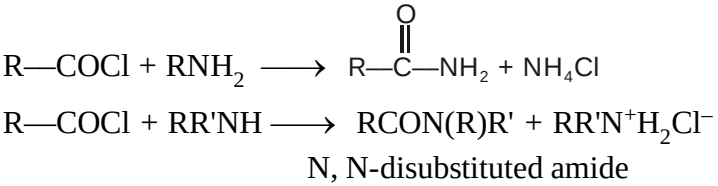
AMIDES ($RCONH_2$)

Structure of amide 

❑ **Method of Preparation :**

1. Amides from Acyl chloride :

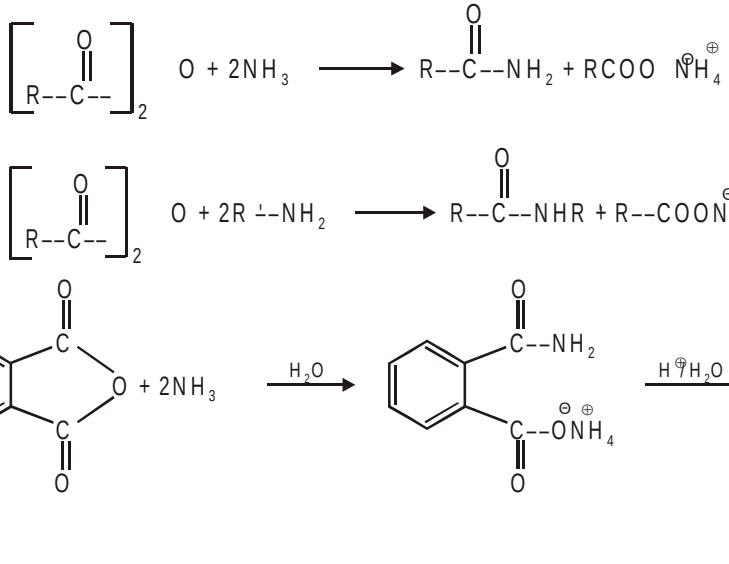
Primary amines, secondary amines and ammonia all react rapidly with acid chloride to form amides. An excess of ammonia or amine is used to neutralize the HCl that would be formed otherwise.



N, N-disubstituted amide

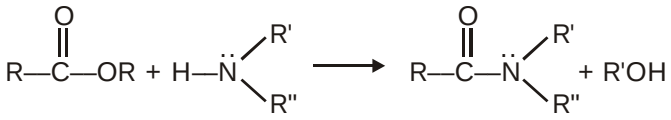
node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & it's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

2. Amides from acid anhydride :

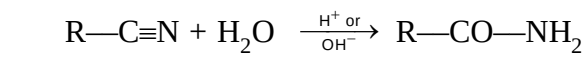


3. From Esters (Ammonolysis) :

Ester undergoes nucleophilic substitution at their acyl carbon by nucleophilic ammonia or its derivative

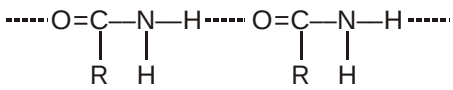


4. By partial hydrolysis of alkyl nitriles :



Physical Properties :

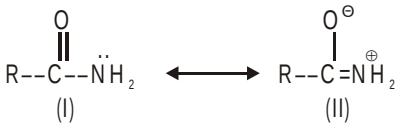
All amides except formamide are crystalline solid at room temperature. They have relatively high melting and boiling point due to association of amide molecules by inter molecular hydrogen bonds.



Chemical Properties :

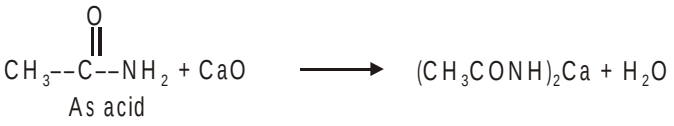
1. Amphoteric character :

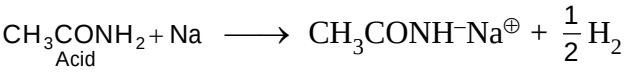
Amides are very feeble bases due to involvement of pair of electron present on N atom in resonance with carboxyl groups. As a result N atom receives partial +ve charges showing feeble acidic character as well



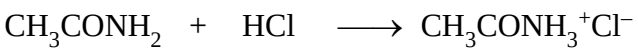
node06\B0B0-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

(i) Acidic character : Due to structure II amide can act as acid.

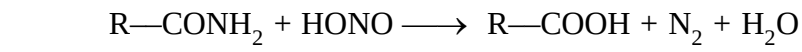




(ii) Basic Character : Due to structure I having lone pair of electrons on N atom it acts as base.



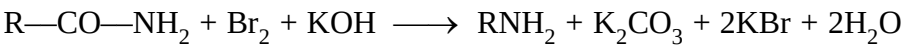
2. Reaction with nitrous acid :

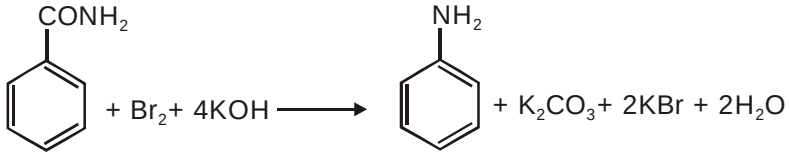


The reaction proceeds via the attack of electrophilic species NO^+ generated from HNO_3.

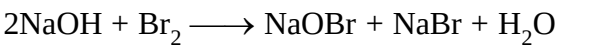
3. Hoffmann's Bromide Reaction :

Amides react with bromine in the presence of alkali to form a primary amine having one carbon atom less than the parent amides.

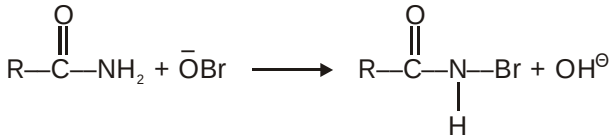




Mechanism :

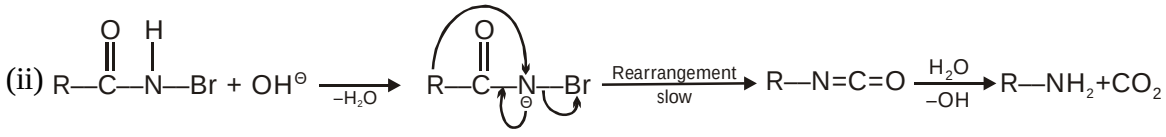


(i)

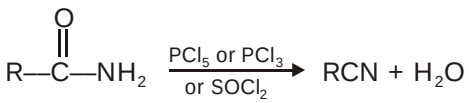


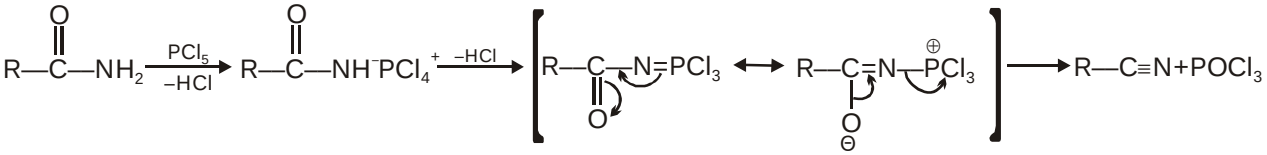
N-bromoacetamide

(ii)



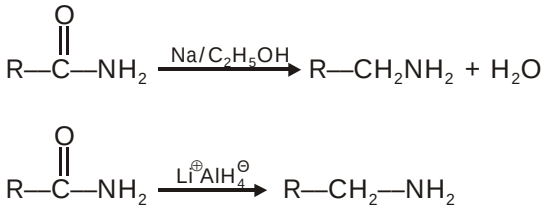
4. Reaction with PCl_5 , PCl_3 or $SOCl_2$:





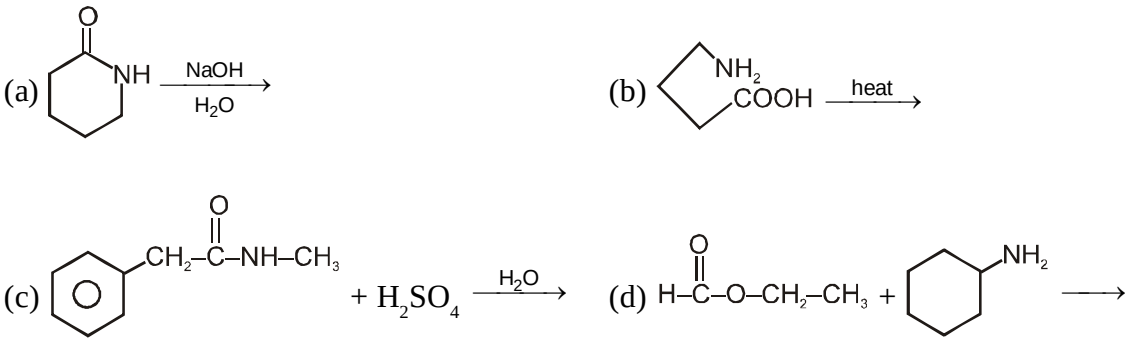
node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & it's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

5. Reduction :



PROBLEMS

1. Predict the products of following reaction

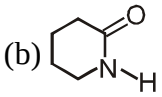


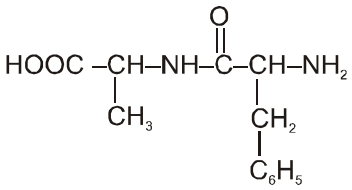
2. Write balanced equation, having all the organic product , for the reaction of phenylacetamide with

(a) hot HCl (aq) (b) hot NaOH (aq)

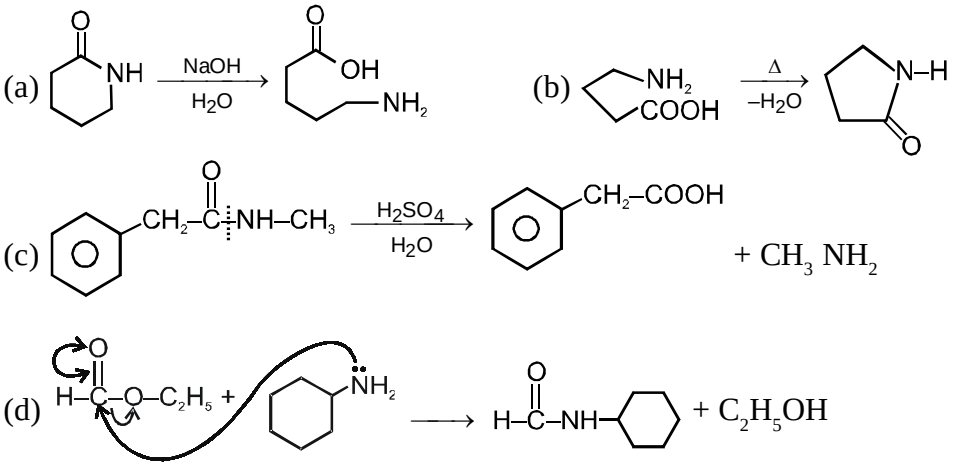
3. What products would you expect from acidic & basic hydrolysis of each of the following amides ?

(a) N,N - Diethylbenzamide





Ans.1



node06\B0B0-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

ALIPHATIC AMINES

Amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by alkyl/Aryl group.

Amines are classified as primary(p) or 1°, secondary(s) or 2° or tertiary(t) or 3° depending on the number of alkyl/Aryl groups attached to nitrogen atom.

$NH_3 \xrightarrow[-H]{+R}$ $R—NH_2$ (p–amine, (amino)) $\xrightarrow[-H]{+R}$ R_2NH (s–amine, (Imino)) $\xrightarrow[-H]{+R}$ $R_3\ddot{N}$ (t–amine, (Nitrilo))

General formula

1° amine	2° amine	3° amine
$C_nH_{2n+1}NH_2$ or $C_nH_{2n+3}N$	$(C_nH_{2n+1})_2NH$	$(C_nH_{2n+1})_3N$

❑ **General Method of Preparation :**

(1) Ammonolysis of alkyl halides and alcohol :

(a) From Ammonolysis of alkyl halides [Hofmann's ammonolysis] :

When an aqueous solution of ammonia is heated with alkyl halide all the three types of amines and quaternary ammonium salt are formed.

$$R—X \xrightarrow[-HX]{NH_3/\Delta} R—NH_2 \xrightarrow[-HX]{R-X} R_2NH \xrightarrow[-HX]{R-X} R_3N \xrightarrow{R-X} R_4N^{\oplus}X^{\ominus}$$

(Quaternary ammonium salt)

If ammonia is taken in excess, 1° amine is the main product.

(b) Ammonolysis of alcohols :

When ROH and NH_3 are passed over Al_2O_3 or ThO_2 at 350° C all the three types of amines are formed.

$$R—OH \xrightarrow[Al_2O_3/400°C]{NH_3} R—NH_2 \xrightarrow[Al_2O_3]{R-OH} R_2NH \xrightarrow[Al_2O_3]{R-OH} R_3N$$

Note : (i) Quaternary ammonium hydroxide is not formed due to steric hindrance.

(ii) If excess of ammonia is used, then main product will be primary amine.

(2) By reduction :

(a) With $RCONH_2$: $RCONH_2 \xrightarrow{LiAlH_4} RCH_2NH_2$

(b) With RCN : $RCN \xrightarrow{Sn/HCl} RCH_2NH_2$

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & it's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

This reaction is called mendius reaction.

The reduction of alkyl isocynides with sodium and ethanol gives secondary amines.

$$R—NC \xrightarrow[\text{or } 4[H]]{C_2H_5OH / Na} RNHCH_3$$

(c) With Oximes : $R—CH{=}N—OH \xrightarrow[Na / C_2H_5OH]{LiAlH_4} RCH_2—NH_2 + H_2O$

(d) With RNO_2 : $RNO_2 \xrightarrow[\text{or } 6[H]]{Sn / HCl} RNH_2 + 2H_2O$

(3) By hydrolysis of :

(a) R—NC : Alkyl isocyanide undergoes hydrolysis with mineral acid and forms alkyl amine.

$$R—NC + 2H_2O \xrightarrow{HCl} RNH_2 + HCOOH$$

(b) RNCO : Alkyl isocyanate undergoes hydrolysis on heating with KOH.

$$R—N{=}CO + 2\ KOH \longrightarrow RNH_2 + K_2CO_3$$

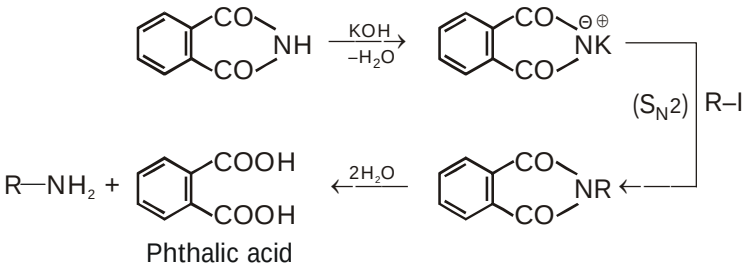
(4) From Grignard reagent :

Alkyl magnesium iodide reacts with chloramine to yield alkyl amine.

$$R—Mg—I + Cl—NH_2 \longrightarrow R—NH_2 + Mg\begin{matrix} I \\ Cl \end{matrix}$$

(5) Gabriel phthalimide synthesis :

Phthalimide is first treated with alcoholic KOH to obtain potassium phthalimide which is then treated with alkyl iodide. Then alkyl phthalimide on hydrolysis yields alkylamine. This method is used in the formation of pure aliphatic primary amines.



Phthalic acid

(6) By Hofmann's bromamide reaction (Hofmann's Hypobromite reaction) : (Discussed earlier)

(7) Curtius reaction :

Acid chloride on treatment with sodium azide give acid azides which on pyrolysis gives isocyanates which on hydrolysis gives corresponding amines.

$$R-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow{NaN_3} \underset{\text{Acyl azide}}{RCON_3} \xrightarrow[\Delta]{-N_2} \underset{\text{Alkyl isocyanate}}{R-N=C=O} \xrightarrow{H_2O} \underset{\text{Alkyl amide}}{R-NH_2}$$

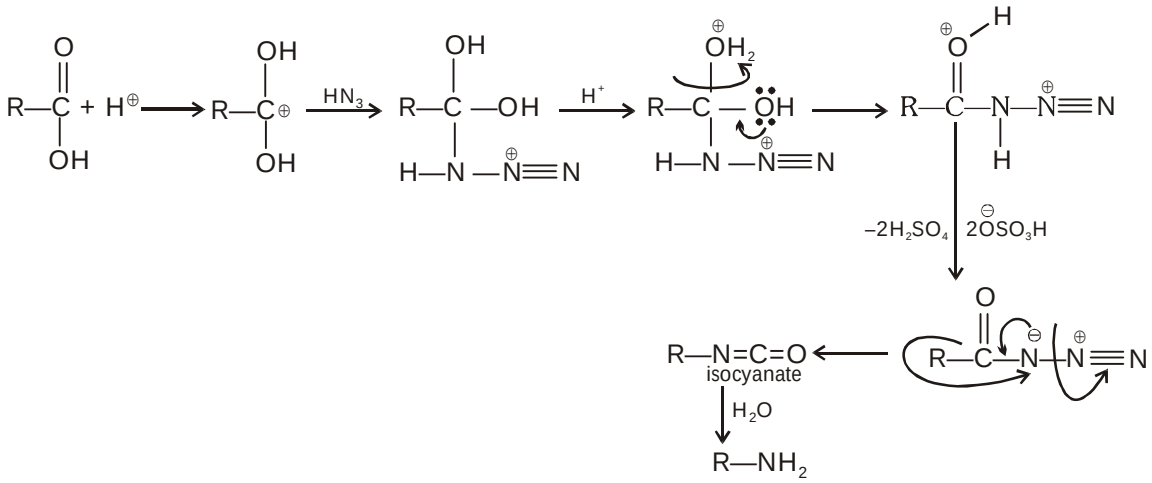
node06\B0B0-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

(8) Schmidt reaction :

In presence of conc. H_2SO_4 alkanoic acid reacts with hydrazoic acid (N_3H) to yield alkylamine.

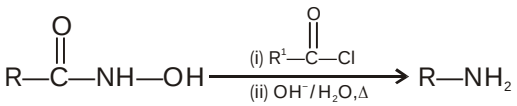
$$R—COOH + N_3H \xrightarrow{\text{Conc. } H_2SO_4} R—NH_2 + N_2 + CO_2$$

Mechanism :



(9) Lossen rearrangement reaction :

In this reaction hydroxamic acid undergoes rearrangement and gives alkyl amine.



(10) Reductive amination of aldehyde and ketone :

$$>C=O + NH_3 + H_2 \xrightarrow[\Delta]{Ni} >CH—NH_2 + H_2O$$
1° amine

$$>C=O + RNH_2 + H_2 \xrightarrow[\Delta]{Ni} >CH—NHR + H_2O$$
2° amine

$$>C=O + R_2NH + H_2 \xrightarrow[\Delta]{Ni} >CH — NR_2 + H_2O$$
3° amine

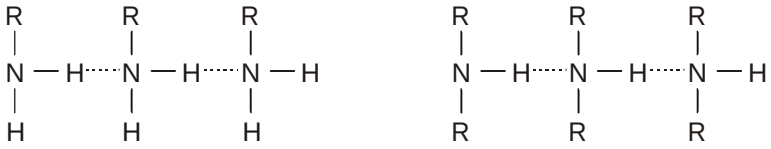
node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & it's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

❑ **Physical Properties :**

(i) CH_3NH_2 is gas and $C_2H_5NH_2$ is a volatile liquid.

(ii) Higher amines have fishy smell.

(iii) H –Bonding (weaker as compared to H—O —H).



(1° amine) (2° amine)

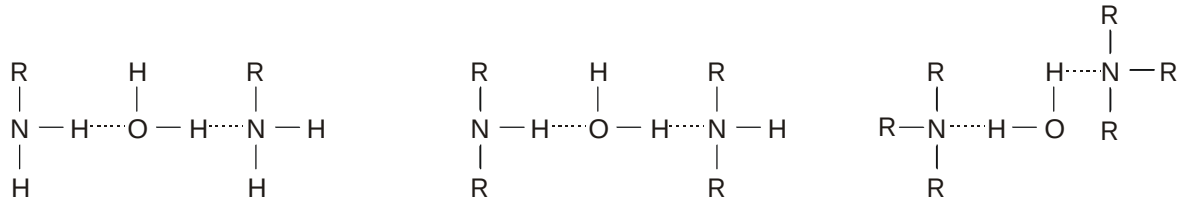
In 3° amine (due to absence of H–atom) H–bonding is not possible.

(iv) **Boiling point :** Due to small intermolecular association the b.p. of 1° and 2° amines are lower than those of alcohols of comparable molecular weight. The boiling point of 3° amines which form no H–bonds are near to those of alkanes of comparable molecular weight.

Boiling point α molecular weight

Order of B.P. :	1° amine	>	2° amine	>	3° amine
so order of volatility ↓	3° amine	>	2° amine	>	1° amine

(v) **Solubility :** Low molecular weight amines (< six carbon) are very soluble in water. The water solubility of amines decreases with increasing size of alkyl group.



(1° amine) (2° amine) (3° amine)

Order of solubility ⟶ p– amine > s– amine > t– amine

❑ **Chemical Properties :**

(i) Basic character of amines is due to the presence of lone pair of electrons on the N - atom.

(ii) Basic strength depends on electron donating tendency.

Basicity order in aqeous solution and in liquid phase. $Et_2NH > Et_3N > EtNH_2$. Due to steric hindrance in 3° amine, it is less basic, than 2° amine.

Steric hindrance of three $-C_2H_5$ group protect the lone pair of nitrogen from the attack of $H^{\oplus}$.

But in gaseous phase basic order is $Et_3N > Et_2NH > EtNH_2$

Some other basic order of different amine if alkyl group would be change

Alkyl groups (R–)	Relative base strength in H_2O
(i) CH_3 –	$R_2NH > RNH_2 > R_3N > NH_3$
(ii) C_2H_5 –	$R_2NH > R_3N > RNH_2 > NH_3$
(iii) $(CH_3)_2CH$ –	$RNH_2 > R_2NH > R_3N > NH_3$
(iv) $(CH_3)_3C$ –	$NH_3 > RNH_2 > R_2NH > R_3N$

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

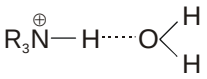
❑ **Special point :**

(I) Tertiary amine is less basic then secondary due to following reasons :

(i) **Steric hindrance :** In tertiary amines (R_3N) , three alkyl groups attached to N are bulkier and as such exert steric hindrance.

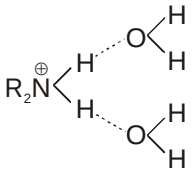
(ii) **Decrease in hydration :**

In tertiary amine



Protonated t–amine can form H–bonding with water molecule only at one point [less stable]

In secondary amine



Protonated s–amine can form H–bonding with water molecules at two points (more stable)

3° amine are less stable as compare to 2° amine due to low hydration so less basic.

(II) The basic strength of aniline is less than aliphatic amines as the lone pair of electron present on N–atom interact with the delocalized π - orbital of benzene ring. Hence it is less available for protonation on N–atom.

The basic order nature for aniline, pyridine and pyrrole ⟶ Pyridine > Aniline > Pyrrole

(2) Reactions showing basic nature :

(a) It reacts with acids to form salts.

$$RNH_2 + HCl \longrightarrow [\overset{\oplus}{R}NH_3]\overset{\ominus}{Cl} \xrightarrow[\text{High temp.}]{\Delta} R{-}Cl + NH_3$$

Alkyl ammonium chloride

(Acidic salt)

$$2RNH_2 \xrightarrow{H_2SO_4} (\overset{\oplus}{R}NH_3)_2\ SO_4^{-2}$$ Alkyl ammonium sulphate

(b) Amines reacts with auric acid and platinic chlorides in presence of HCl to form double salts.These double salts decompose on ignition to pure metal. Therefore the formation and decomposition of the double salts is used for determining the molecular weight of amines.

$$2R{-}NH_2 + \underbrace{PtCl_4 + 2HCl} \longrightarrow [\overset{\oplus}{R}NH_3]_2PtCl_6^{-2}$$

(chloro platinic acid) Alkyl ammonium chloroplatinate

$$RNH_2 + \underbrace{AuCl_3 + HCl} \longrightarrow [\overset{\oplus}{R}NH_3]\overset{\ominus}{AuCl_4}$$

[Chloroauric acid] Alkyl ammonium chloroaurate

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & it's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

(c) **Reaction with H_2O :** It forms alkyl ammonium hydroxide with water ammonium hydroxides are used for precipitation of II[nd] and III[rd] group cations in qualitative analysis

$$RNH_2 + H_2O \longrightarrow \overset{\oplus}{(RNH_3)}\overset{\ominus}{O}H$$

Base

$$FeCl_3 + 3[\overset{\oplus}{RNH_3}]\overset{\ominus}{O}H \longrightarrow Fe(OH)_3 + 3[\overset{\oplus}{RNH_3}]\overset{\ominus}{Cl}$$

Brown ppt

$$AlCl_3 + 3[\overset{\oplus}{RNH_3}]\overset{\ominus}{O}H \longrightarrow Al(OH)_3 + 3[\overset{\oplus}{RNH_3}]\overset{\ominus}{Cl}$$

White ppt.

$$CrCl_3 + 3[\overset{\oplus}{RNH_3}]\overset{\ominus}{O}H \longrightarrow Cr(OH)_3 + 3[\overset{\oplus}{RNH_3}]\overset{\ominus}{Cl}$$

Green ppt.

(3) Reaction with alkyl halides :

Alkyl amine reacts with alkyl halides and form sec., ter. amines and quaternary ammonium salt.

$$RNH_2 + R{-}X \xrightarrow{-HX} R_2NH \xrightarrow[-HX]{RX} R_3N \xrightarrow{RX} \overset{\oplus}{R_4N}\overset{\ominus}{X}$$

◆ **Special Point :**

Separation of 1°, 2° and 3° amines :

1°, 2°, 3° amine + $R_4NX \xrightarrow{\text{distillation}}$ Mixture of 1°, 2°, 3° amine

R_4NX does not undergo distillation.

Mixture of 1°, 2°, 3° amine can be separated by following methods.

(i) Fractional distillation : The mixture of amines may be separated by fractional distillation because their boiling points are quite different. It is used in industry.

(ii) Hinsberg method : In this method mixture of amines is seperated by using benzene sulphonyl chloride (Hinsberg's reagent).

$C_6H_5SO_2Cl$ + 1° amine $\longrightarrow$ Product $\xrightarrow{KOH}$ dissolve

$C_6H_5SO_2Cl$ + 2° amine $\longrightarrow$ Product $\xrightarrow{KOH}$ insoluble

3° amine does not react with benzene sulphonyl chloride.

(iii) Hofmann method : In this method mixture of amines is separated by using ethyl oxalate.

1° amine + ethyl oxalate $\longrightarrow$ solid product

2° amine + ethyl oxalate $\longrightarrow$ liquid product

3° amine + ethyl oxalate $\longrightarrow$ No reaction

(4) Acetylation : Acetylation takes place when alkyl amine combines with acetyl chloride or acetic anhydride.

$$RNH_2 + ClCOCH_3 \longrightarrow RNHCOCH_3 + HCl$$

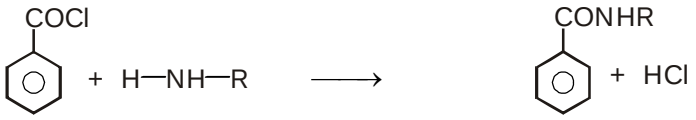
(N –alkyl acetamide)

$$RNH_2 + (CH_3CO)_2O \longrightarrow RNHCOCH_3 + CH_3COOH$$

(N –alkyl acetamide)

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

(5) Benzoylation (Schotten baumann reaction) :



Benzoylchloride N–alkyl benzamide

(6) Acidic nature : Amines are very weak acids only 1° and 2° amines show acidic nature.

$$R—NH_2 + Na \longrightarrow R\overset{\ominus}{N}H\overset{\oplus}{N}a + \frac{1}{2}H_2$$

N– alkyl sodamide

(7) Reaction with Tilden reagent :

When alkylamine reacts with nitrosyl chloride (Tilden reagent) alkyl chloride is formed. This reaction is important in interconversion.

$$R—NH_2 + NOCl \longrightarrow RCl + N_2 + H_2O$$

(8) Reaction with phosgene :

$$R—NH_2 + COCl_2 \longrightarrow R—N=C=O + 2HCl$$

Alkyl isocyanate

(9) Reaction with halogen : The hydrogen atoms of the amino group are replaced by halogen atoms in presence of alkali solution.

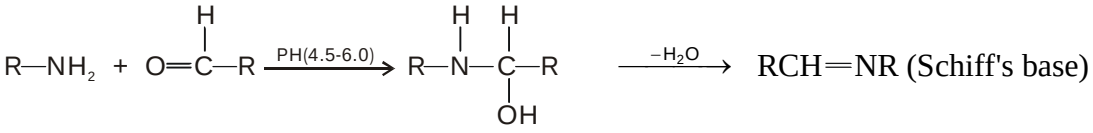
$$R—NH_2 + Br_2 \xrightarrow[\text{or KOH},\Delta]{NaOH} R—NH—Br + HBr$$

N– bromo alkylamine

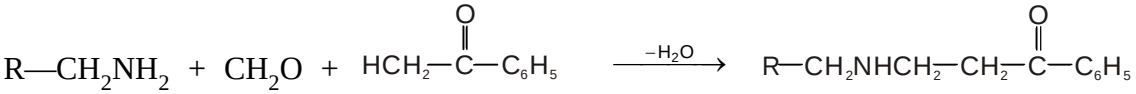
$$R—NH—Br + Br_2 \xrightarrow[\Delta]{NaOH} R—NBr_2 + HBr$$

N, N–dibromo alkyl amine

(10) Reaction with aldehydes : Alkylamine reacts additively with aldehydes to form α - hydroxyl amines which are changed to schiff bases with elimination of water molecule.



(11) Mannich reaction :



Acetophenone Mannich base

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & it's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

(12) Oxidation :

- **$KMnO_4/H^+$:** Alkylamine on oxidation with acidified potassium permaganate forms aldimine which on hydrolysis gives aldehyde and ammonia.

$$R—CH_2NH_2 \xrightarrow[KMnO_4 / H^+]{[O]} R-C(=O)-OH$$

$$R_2CHNH_2 \xrightarrow{[O]} \underset{\text{(Ketimine)}}{R_2C=NH} \xrightarrow[H^+]{H_2O} \underset{\text{(Ketone)}}{R_2C=O} + NH_3$$

$$R_3CNH_2 \xrightarrow{[O]} R_3CNO_2 \text{ (Nitroalkane)}$$

- **With H_2SO_5 (Caro's acid) Or H_2O_2/Fe^{+2} (Fenton reagent) :**

$$RCH_2NH_2 \xrightarrow{[O]} \underset{\text{N-alkyl hydroxylamine}}{R—CH_2—NH—OH} + \underset{\text{Aldoxime}}{RCH=NOH} + \underset{\text{Hydroxamic acid}}{R—C(=O)—NHOH}$$

$$R_2CH\ NH_2 \xrightarrow{[O]} R_2C=N—OH \text{ (Ketoxime)}$$

$$R_3CNH_2 \xrightarrow{[O]} R_3CNO \text{ (Nitroso compound)}$$

(13) Carbylamine Reaction (Iso cyanide test) :

When alkyl amine's heated with chloroform and alc. KOH alkyl isocyanide is formed which has very bad smell.

This test is also given by aniline . This is a test for p– amines.

$$R—NH_2 + CHCl_3 + 3\ KOH \longrightarrow R — N \equiv C + 3KCl + 3H_2O$$

Nucleophile RNH_2 attacks electrophilic intermediate [$:CCl_2$] dichlorocarbene.

Mechanism :

$$CHCl_3 + \overset{\ominus}{O}H \xrightarrow{-H_2O} Cl—\overset{\ominus}{C}(Cl)—Cl \xrightarrow{-\overset{\ominus}{Cl}} :CCl_2$$

Dichlorocarbene

$$R—\ddot{N}H_2 + :CCl_2 \xrightarrow{r.d.s} R—\overset{\oplus}{N}H—\overset{\ominus}{C}(Cl)—Cl \xrightarrow{-HCl} R—\overset{\oplus}{N}H=\overset{\ominus}{C}—Cl \longrightarrow R—N\equiv C$$

(14) Hofmann's mustard oil test :

When alkyl amine is heated with carbon disulphide and mercuric chloride alkyl isothiocyanate is formed which has smell like mustard oil.

$$R—NH_2 + S=C=S \longrightarrow R—NH—C(=S)—SH \xrightarrow{HgCl_2} \underset{\text{Alkyl isothiocyanate}}{R—N=C=S} + HgS + 2HCl$$

$$R_2NH + S=C=S \longrightarrow R_2N—C(=S)—SH \xrightarrow{HgCl_2} \text{No reaction}$$

$$R_3N + S=C=S \longrightarrow \text{No reaction.}$$

node06\B0B0-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

Ex. Which statement is not true for primary amines

(A) These forms salt will acids (B) Gives alcohols on hydrolysis

(C) Gives carbyl amine reaction (D) Gives musturd oil test

Sol. (B)

(15) Reaction with HNO_2 ($NaNO_2$ + HCl or H_2SO_4) :

(a) Primary amines react with nitrous acid to produce nitrogen gas [seen as bubbles]

$R—NH_2 + HONO \longrightarrow R—OH + N_2\uparrow + H_2O$

$CH_3NH_2 + HNO_2 \longrightarrow CH_3—O—CH_3$

(b) $R_2NH + HONO \longrightarrow R_2N—NO + H_2O$

N–nitroso amine (Yellow oily layer)

This is called **libbermann's** nitroso test

(c) $R_3N + HONO \longrightarrow R_3\overset{\oplus}{N}H\overset{\ominus}{N}O_2$ Trialkyl ammonium nitrite (Soluble in water)

❑ **Points to Remember :**

(i) Nitrosoamines are carcinogens (Cancer causing agents)

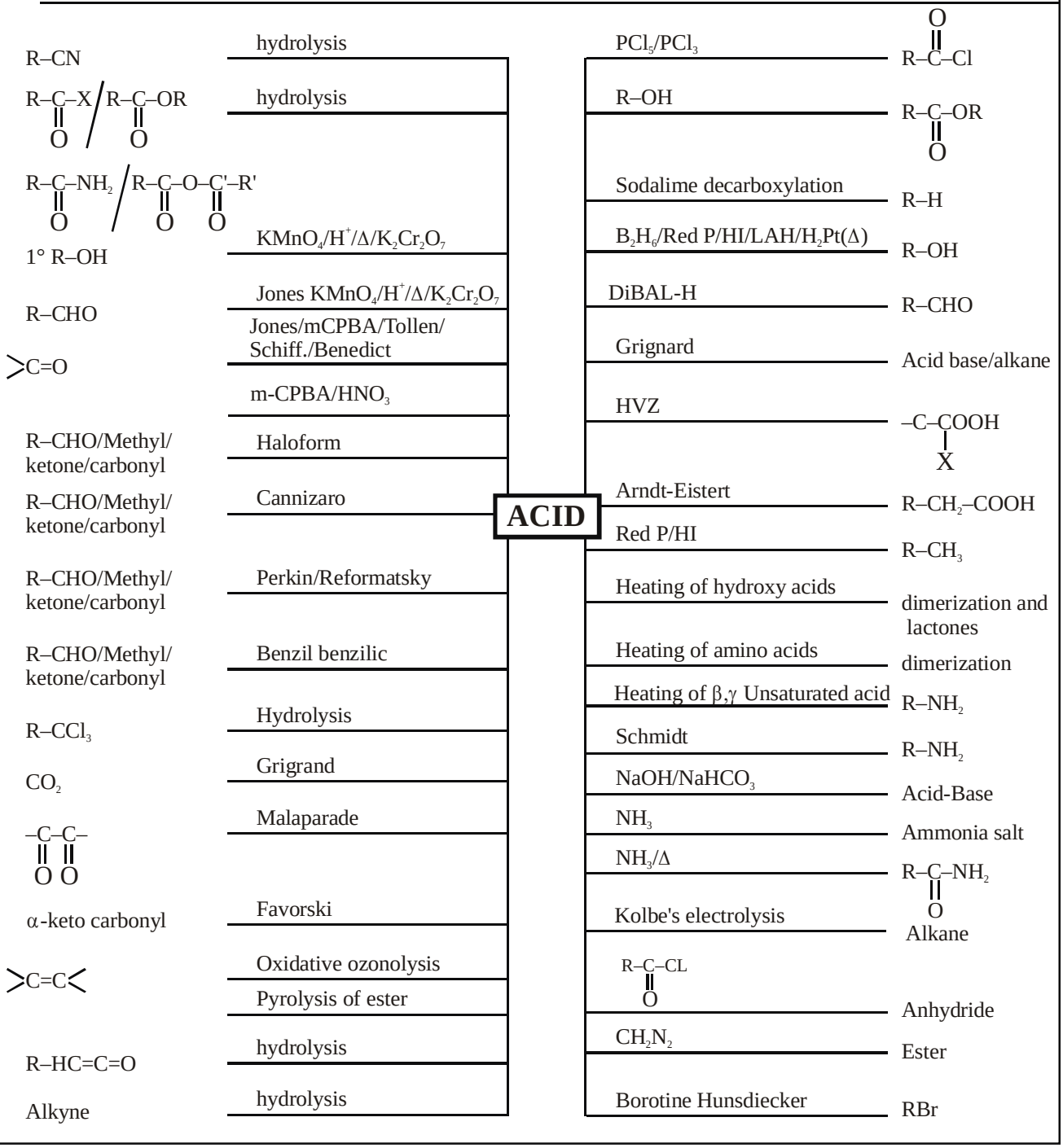
(ii) Amines can have chiral N-atom but cannot be resolved into enantiomeric forms because of rapid inversion of one enantiomeric form into the other.

(iii) The Schiff's bases formed by reaction of 1°-amines and aldehyde/ketones are also called anils.

(iv) In Hoffmann test $CS_2 + HgCl_2$ are used and in Hinsberg test benzene sulphonyl chloride ($C_6H_5SO_2Cl$) is used.

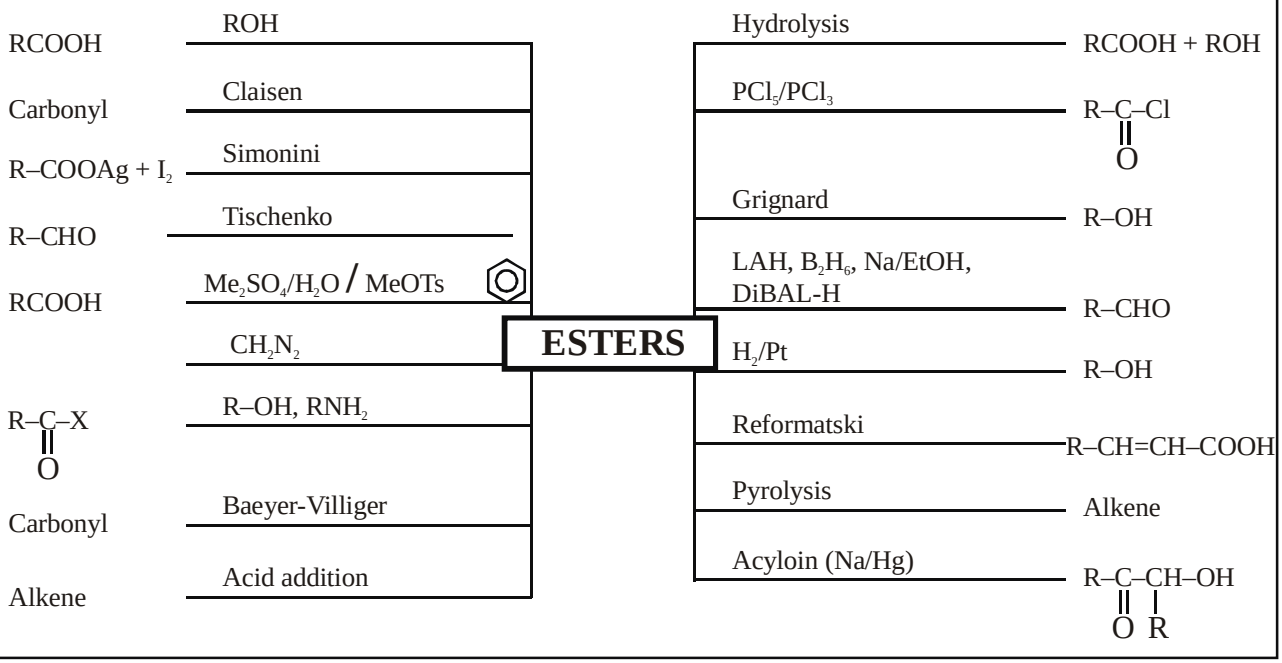
node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & it's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

FLOW CHART FOR CARBOXYLIC ACID

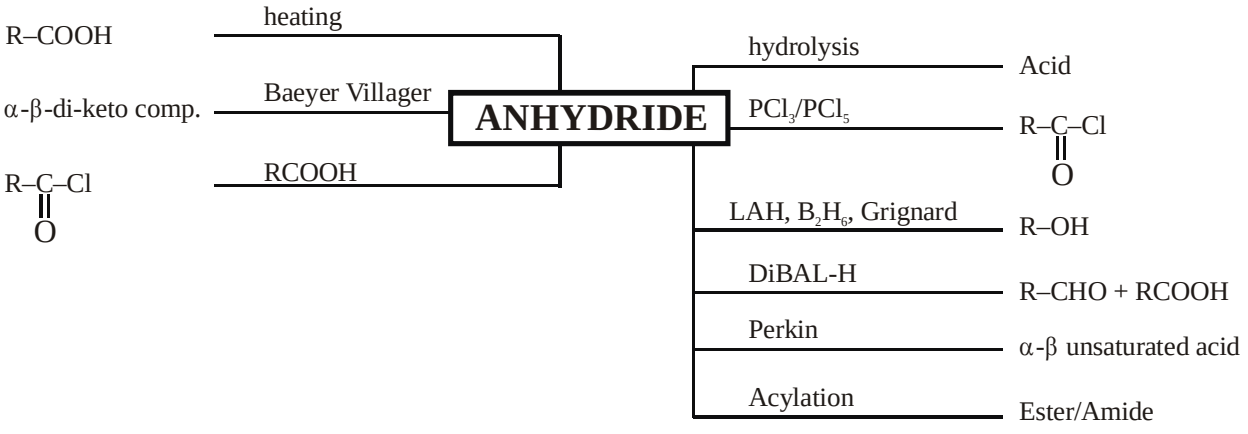


node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

FLOW CHART FOR ESTERS

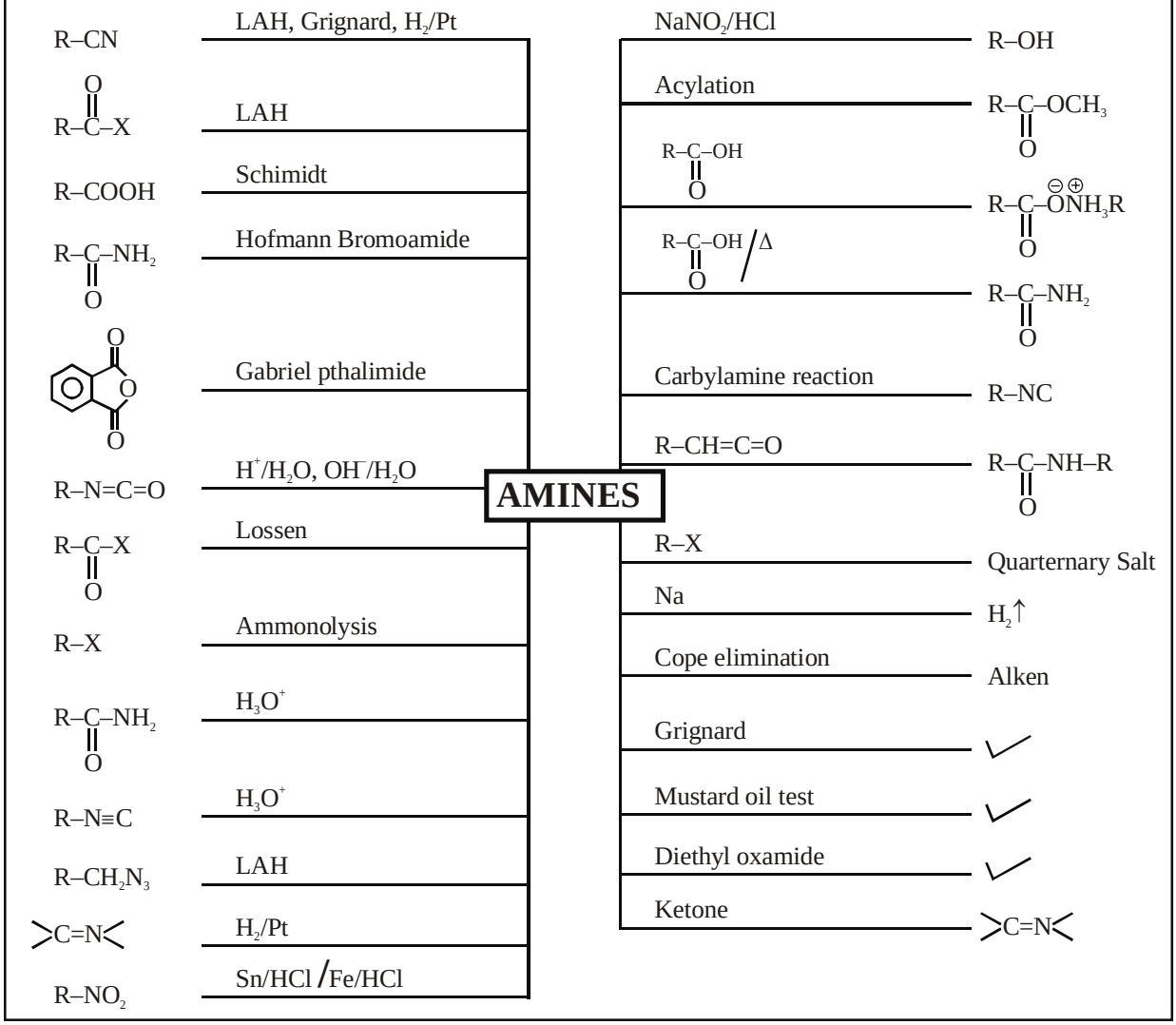


FLOW CHART FOR ANHYRIDE



node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & it's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

FLOW CHART FOR AMINES



node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\01_Carboxylicacid & amines_(Theory).p65

CARBOXYLIC ACIDS AND IT'S DERIVATIVE, ALIPHATIC AMINES

EXERCISE # O-I

1. In which reaction product is hydrocarbon ?

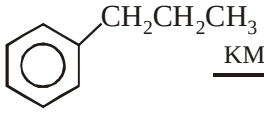
(A) $RCOOK \xrightarrow{\text{Electrolysis}}$ (B) $RCOOAg \xrightarrow{I_2/\Delta}$

(C) $CH_3–CH_3 \xrightarrow{Cl_2/h\nu}$ (D) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Cl \xrightarrow{C_2H_5OH}$

CA0001

2. Which of the following set of reaction can not prepare carboxylic acid as the final product :

(A) $R–MgX + O=C=O \xrightarrow{\text{dry ether}} A \xrightarrow{H_3O^+}$ (B) $R–CN \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } SnCl_2+HCl}$

(C)  $\xrightarrow[\Delta]{KMnO_4,\overset{\ominus}{O}H} A \xrightarrow{H_3O^+}$ (D) $CH_3(CH_2)_8CH_2OH \xrightarrow[H_2SO_4]{CrO_3}$

CA0002

3. In the given reaction,

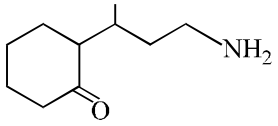
$$C_6H_5-\overset{\displaystyle O}{\overset{||}{C}}-CH_3 \xrightarrow[\text{(ii) } H^{\oplus}]{\text{(i) } Br_2/KOH} CHBr_3 + [X]$$

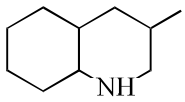
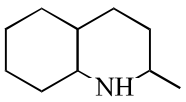
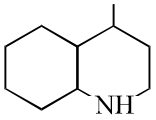
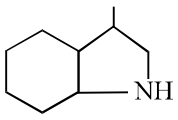
[X] will be :

(A) $C_6H_5–CHO$ (B) C_6H_5COOH (C) $C_6H_5–CH_2OH$ (D) CH_3COOH

CA0003

4. Reductive amination of A forms:

A : 

(A)  (B)  (C)  (D) 

CA0004

5. In the given reaction :

[X] + Acetic anhydride $\longrightarrow$ Aspirin

[X] will be :

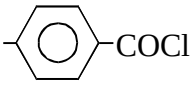
(A) Benzoic acid (B) *o*-methoxybenzoic acid

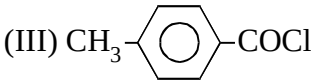
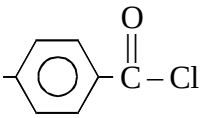
(C) *o*-Hydroxybenzoic acid (D) *p*-Hydroxybenzoic acid

CA0005

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & its Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & its Derivative, Aliphatic Amines (ENG).p65

6. Arrange following compounds in decreasing order of reactivity for hydrolysis reaction :

(I) C_6H_5COCl (II) 

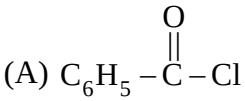
(III)  (IV) 

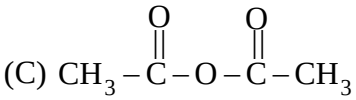
(A) II > IV > I > III (B) II > IV > III > I

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

CA0006

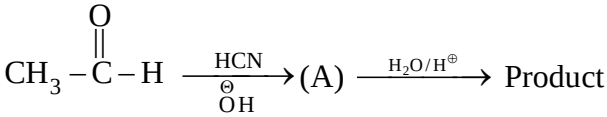
7. Which one of the following compounds gives carboxylic acid with HNO_2?

(A)  (B) $C_6H_5CONH_2$

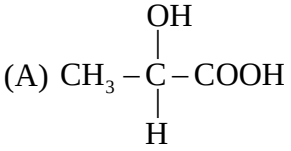
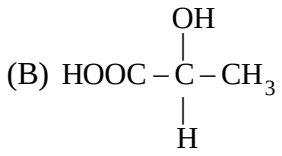
(C)  (D) $CH_3COOC_2H_5$

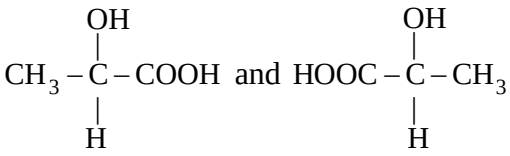
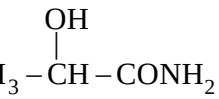
CA0007

8. In the reaction sequence ,



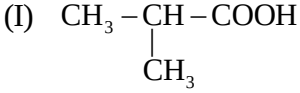
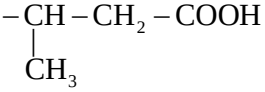
Product will be :

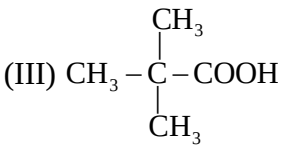
(A)  (B) 

(C) Mixture of  (D) 

CA0008

9. Arrange these esters in decreasing order of ease of esterfication with $CH_3OH/H^{\oplus}$:

(I)  (II) 

(III)  (IV) $(CH_3–CH_2)_3C–COOH$

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

CA0009

node06\B0B0-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & It's Derivative, Aliphatic Amines (ENG).p65

10. Which optically active compound on reduction with $LiAlH_4$ will give optically inactive compound?

(A) $CH_3-\underset{\underset{OCH_3}{|}}{CH}-COOH$ (B) $CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-COOH$

(C) $CH_3-CH_2-\underset{\underset{CH_2OH}{|}}{CH}-COOH$ (D) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-COOH$

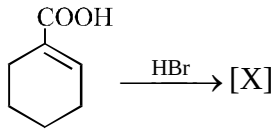
CA0010

11. Which will form lactone on treatment with NaOH ?

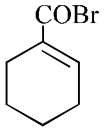
(A) α-Bromo acid (B) β-Bromo acid (C) β-Hydroxy acid (D) δ-Bromo acid

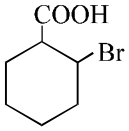
CA0011

12. In the given reaction:

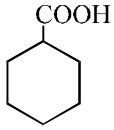


[X] will be :

(A) 

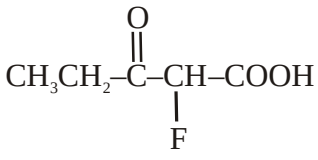
(B) 

(C) 

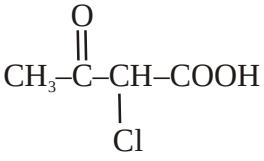
(D) 

CA0012

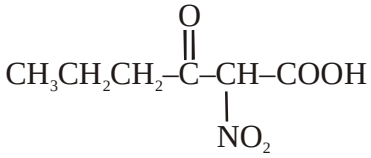
13. Correct order of decarboxylation



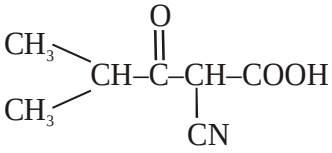
(a)



(b)



(c)



(d)

(A) a > b > c > d (B) c > d > b > a (C) c > d > a > b (D) d > c > a > b

CA0013

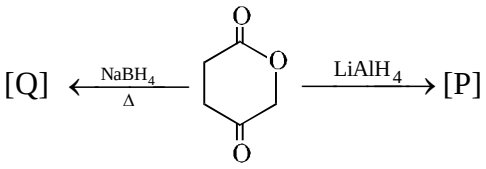
node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & its Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & its Derivative, Aliphatic Amines (ENG).p65

14. N-Ethyl pthalimide on hydrolysis gives:

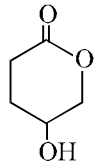
(A) Methyl alcohol (B) Ethyl amine (C) Dimethyl amine (D) Diethyl amine

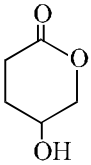
CA0014

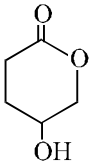
15. In the given reaction:



[P] and [Q] respectively be :

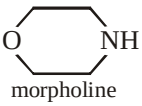
(A) $CH_2OH-CH_2-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2OH$ and 

(B)  and $CH_2OH-CH_2-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2OH$

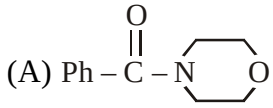
(C) Both are 

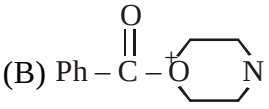
(D) Both are $CH_2OH-CH_2-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2OH$

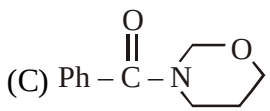
CA0015

16. $Ph-\overset{\overset{O}{||}}{C}-Cl$ +  $\longrightarrow$ A (Major) 'A' is

morpholine

(A) 

(B) 

(C) 

(D) $Ph-\overset{\overset{O}{||}}{C}-NH_2$

CA0016

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & It's Derivative, Aliphatic Amines (ENG).p65

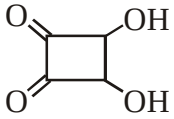
17. $CH_3NH_2 \xrightarrow{(CH_2)_2O} (A)$

(A) 'A' is more basic than CH_3NH_2 (B) 'A' is less basic than CH_3NH_2

(C) 'A' is Ter-amine (D) None

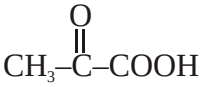
CA0017

18. Which of the following can released CO_2 with $NaHCO_3$.



(i)

$CH_2(COOH)_2$ (ii)

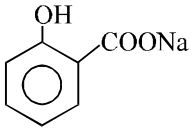
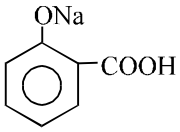
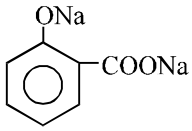


(iii)

(A) (i), (ii) & (iii) (B) (i) & (ii) (C) (ii) & (iii) (D) (i) & (ii)

CA0018

19. Sodium bicarbonate reacts with salicylic acid to form :

(A) C_6H_5ONa (B)  (C)  (D) 

CA0019

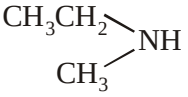
20. Which of the following diazonium salt is relatively stable at 0-5°C:

(A) $CH_3–N\equiv N\}^{\oplus}Cl^-$ (B) $(CH_3)_2CH–N\equiv N\}^{\oplus}Cl^-$

(C) $C_6H_5–N\equiv N\}^{\oplus}Cl^-$ (D) $(CH_3)_3C–N\equiv N\}^{\oplus}Cl^-$

CA0020

21. Which is most volatile ?

(A) $CH_3CH_2CH_2NH_2$ (B) $(CH_3)_3N$ (C)  (D) CH_3OH

CA0021

22. $C_6H_5CONH_2 \xrightarrow{Br_2/OD^{\ominus}} P$, 'P' is :

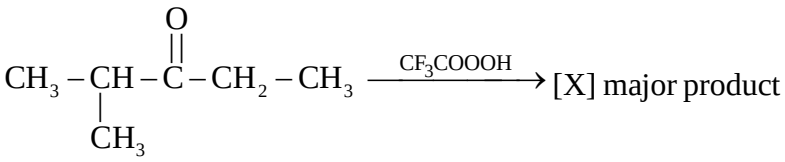
(A) $C_6H_5COND_2$ (B) $C_6H_5ND_2$

(C) C_6H_5NHD (D) $C_6H_5NH_2$

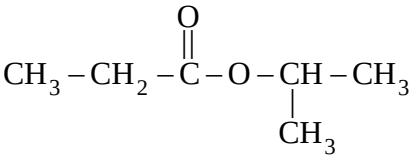
CA0022

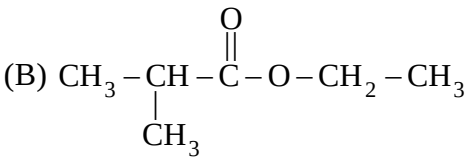
node06\B0B0-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & its Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & its Derivative, Aliphatic Amines (ENG).p65

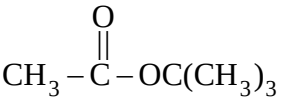
23. In the given reaction:



[X] will be:

(A) 

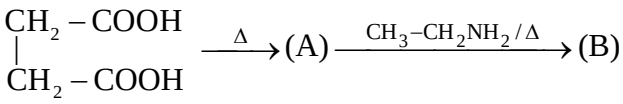
(B) 

(C) 

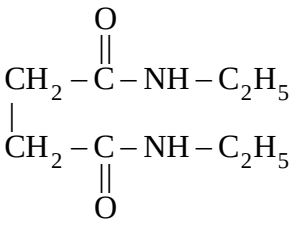
(D) $(CH_3)_3COOCH_3$

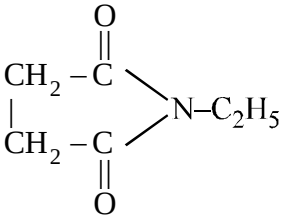
CA0023

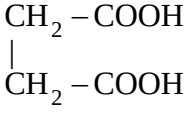
24. In the given reaction sequence:

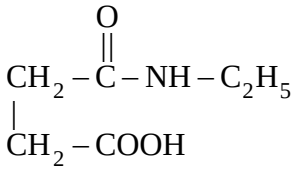


(B) will be:

(A) 

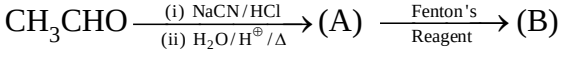
(B) 

(C) 

(D) 

CA0024

25. In the given reaction :



(B) will be :

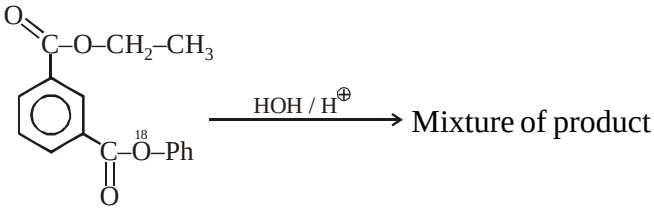
(A) Acetic acid (B) Oxalic acid (C) Pyruvic acid (D) Citric acid

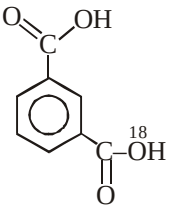
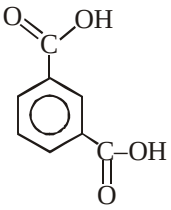
CA0025

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & It's Derivative, Aliphatic Amines (ENG).p65

EXERCISE # O-II

1. Which of the following is/are present in mixture of product :



(A) $CH_3–CH_2–OH$ (B)  (C) $Ph–\overset{18}{O}H$ (D) 

CA0026

2. Mixture of 1°, 2° and 3° amines can be separated by:

(A) Hinsberg's method (B) Hofmann's isocyanide test

(C) Fractional distillation (D) $NaNO_2$ HCl

CA0027

3. RCOOR' can be prepared by:

(A) Esterification of RCOOH

(B) Reaction of $CH_3CH=CH_2$ with methanol

(C) Baeyer-Villiger oxidation of RCOR' with peroxy acid

(D) reaction of RCOCl with R'OH

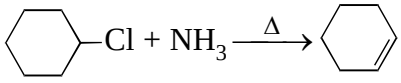
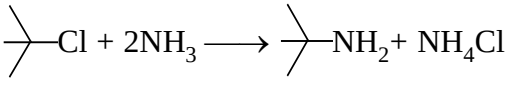
CA0028

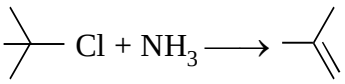
4. Which of the following amine reacts with Hinsberg reagent to give base soluble product :-

(A) Neopentyl amine (B) sec propyl amine (C) diethyl amine (D) ethyl methyl amine

CA0029

5. Which is/are correct reaction(s):

(A)  (B) 

(C)  (D) 

CA0030

6. Which of the following will form acetyl chloride with PCl_5?

(A) MeCOOH (B) MeCOOMe (C) MeCOOCOMe (D) $Me–CONH_2$

CA0031

7. Sodium salt of which compound on electrolysis does not give hydrocarbon:

(A) C_6H_5COOH (B) HCOOH (C) $Me_3C–COOH$ (D) COOH–CH=CH–COOH

CA0032

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & its Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & its Derivative, Aliphatic Amines (ENG).p65

8. Among the following, which statement is not correct ?

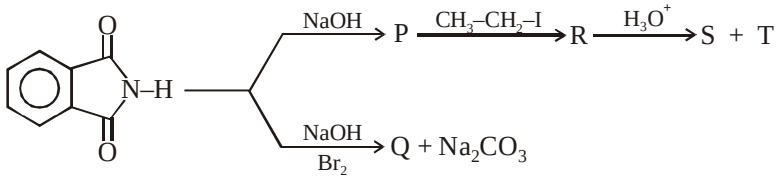
(A) $H_3C—\overset{\overset{O}{\|}}{C}—OH$ will not respond to haloform test

(B) Schiff's regent and Schiff's base are different compounds

(C) Fehling's solution is a good reagent to detect aromatic aldehydes

(D) Both aldehyde and ketone can react with 2,4-dinitrophenylhydrazise reagent

CA0033

9. 

If T can evolve effervescence of CO_2 with a $NaHCO_3$, then correct statement(s) is/are :

(A) S & Q can be distinguished by dye azo test

(B) T is most acidic among all isomeric benzenoid dicarboxylic acid

(C) Q & S can be distinguished by mustered oil test

(D) P, Q & T all are soluble in a $NaHCO_3$

CA0034

10. Acetic anhydride and ammonia gives the product:

(A) CH_3CONH_2 (B) $CH_3CONHCH_3$ (C) CH_3CN (D) CH_3COONH_4

CA0035

11. $CH_3—\overset{\overset{O}{\|}}{C}—O—CH_2—CH_3 \underset{}{\overset{^{18}HOH / H^{\oplus}}{\rightleftharpoons}}$ Ethanoic acid + Ethanol

Isotopic oxygen of water will be present with

(A) Ethanoic acid

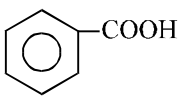
(B) Ethanol

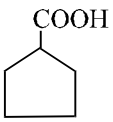
(C) After some time it will also be present in some molecules of ester

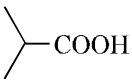
(D) None of these

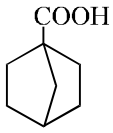
CA0036

12. Which one of the following compounds will give HVZ reaction?

(A) 

(B) 

(C) 

(D) 

CA0037

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & It's Derivative, Aliphatic Amines (ENG).p65

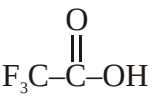
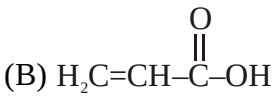
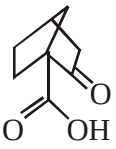
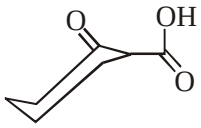
13. $RCH_2CONH_2 + NaOBr \longrightarrow ?$

Rate of reaction will be faster if 'R' is

(A) CH_3- (B) C_2H_5- (C) NO_2- (D) $CN-$

CA0038

14. Which of the following carboxylic acids do not undergo decarboxylation simply on heating ?

(A)  (B)  (C)  (D) 

CA0039

15. Which of the following compounds will give acetic acid with $KMnO_4/H^{\oplus}/\Delta$:

(A) CH_3-CHO (B) $CH_3-CH=CH-CH_3$

(C) $CH_3-C\equiv C-CH_3$ (D) CH_3CH_2OH

CA0040

16. Hofmann degradation is given by:

(A) Succinimide (B) Acid chloride (C) Acid anhydride (D) Acetamide

CA0041

17. The presence of primary amine can be confirmed by its reaction with :

(A) HNO_2 (B) $CHCl_3$ + NaOH (C) CS_2 & $HgCl_2$ (D) H_2SO_4

CA0042

18. Total number of compounds which are soluble in hot a NaOH are :

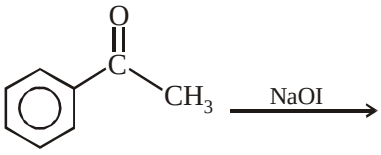
(i) Salicyclic acid (ii) Aspirine (iii) Carbolic acid (iv) Acetic acid

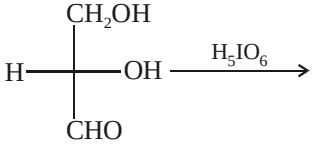
(v) Succinic anhydride (vi) Cyclohexanone (vii) Benzene sulphonamide (viii) Cyclohexene

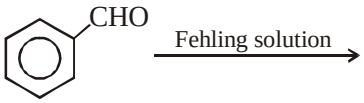
(A) 5 (B) 6 (C) 7 (D) 8

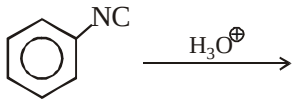
CA0043

19. Number of oxidation reactions in which organic reactant gets oxidised & one of the major product is carboxylic acid/salt :

(A) 

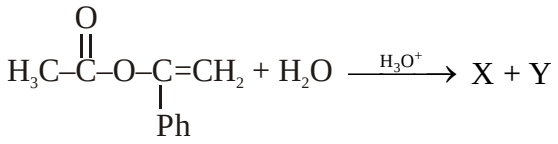
(B) 

(C) 

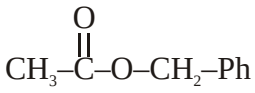
(D) 

CA0044

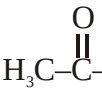
node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & its Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & its Derivative, Aliphatic Amines (ENG).p65

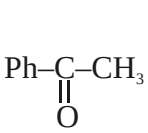
20. 

X and Y are :

(A) X is 

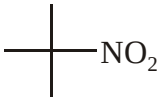
(B) Y is PhCHO

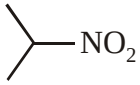
(C) Y is 

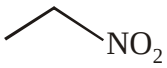
(D) X is 

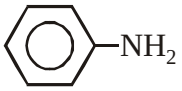
CA0045

21. Which of the following compound react with HNO_2 :

(A) 

(B) 

(C) 

(D) 

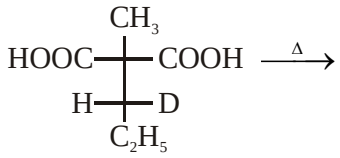
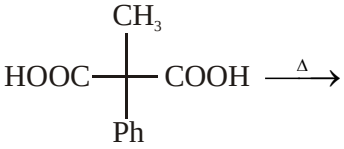
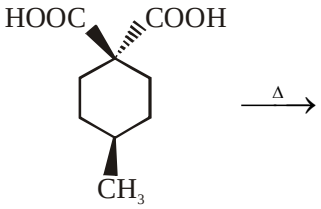
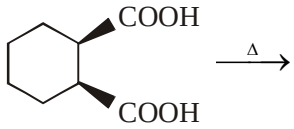
CA0046

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & It's Derivative, Aliphatic Amines (ENG).p65

EXERCISE # S-I

Matching Type Questions

1. Match the following question :

Column - I **(Reaction)**	**Column-II** **(Products)**
(A) 	(P) Diastereomers
(B) 	(Q) Racemic mixture
(C) 	(R) Meso comp.
(D) 	(S) CO_2 gas will evolve

CA0047

2. Match the following question :

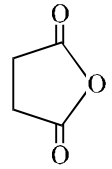
Column I **(Organic compounds oxidised by HIO_4)**	**Column II** **(Products of HIO_4 oxidation)**
(A) CH_3COCHO	(P) PhCH = O + HCOOH
(B) 1,2-cyclohexane dione	(Q) $CH_3CH_2CHO + HOOCCH_3$
(C) PhCH (OH) CHO	(R) HOOC $(CH_2)_4COOH$
(D) CH_3CH_2CH (OH) $COCH_3$	(S) $CH_3COOH + HCOOH$

CA0048

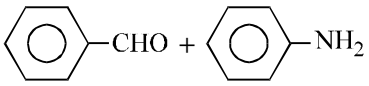
node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & It's Derivative, Aliphatic Amines (ENG).p65

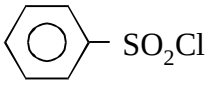
3. Match the following question :

Column I (Reactions)

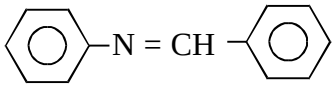
(A) CH_3NH_2 + 

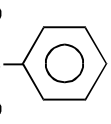
(B) $(CH_3)_2NH + C_6H_5COCl$

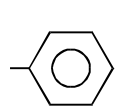
(C) 

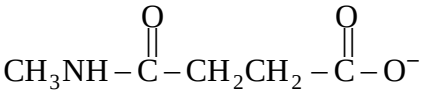
(D) CH_3NH_2 + 

Column II (Products)

(P) 

(Q) $CH_3 - NH-$ 

(R) 

(S) 

CA0049

4. Match the following question :

Column I
(Correct about product)

(A) $R - CN \xrightarrow{H_3O^+}$

(B) $R - NH_2 \xrightarrow[KOH]{CHCl_3}$

(C) $R - NH_2 \xrightarrow[HCl]{NaNO_2}$

(D) $R_2NH \xrightarrow[HCl]{NaNO_2}$

Column II

(P) Product is yellow oily liquid

(Q) Gives red colour with CAN

(R) Gives fruity smell with CH_3OH

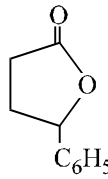
(S) Foul smelling compound is formed.

CA0050

5. Match the following question :

Column I

(A) $PhCONH_2 \longrightarrow Ph–C\equiv N$

(B)  $\longrightarrow CH_2OH–(CH_2)_2–CHOH–C_6H_5$

(C) $CH_3–\underset{\underset{O}{\|}}{C}–OCH_3 \longrightarrow CH_3CH=O$

(D) $CH_3COCl \longrightarrow CH_3–CHO$

Column II

(P) P_2O_5

(Q) $LiAlH_4$

(R) $H_2/Pd–BaSO_4$

(S) DIBALH

CA0051

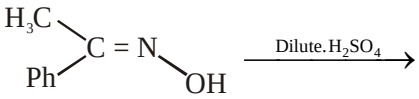
node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & It's Derivative, Aliphatic Amines (ENG).p65

6. Match the following question :

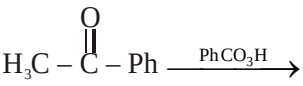
Column I	**Column II**
(A) $RCN \xrightarrow{\text{reduction}}$	(P) 1° Amine
(B) $RCN \xrightarrow[(ii)\,H_2O]{(i)\,CH_3MgBr}$	(Q) Alcohol
(C) $RNC \xrightarrow{\text{hydrolysis}}$	(R) Ketone
(D) $RNH_2 \xrightarrow{HNO_2}$	(S) Acid

CA0052

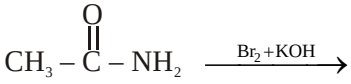
7. Find out number of reactions which involve electron dificient nitrogen [Nitrene character] during reaction mechanism.

(a) 

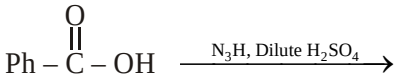
CA0053

(b) 

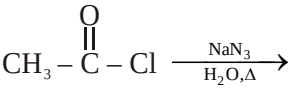
CA0054

(c) 

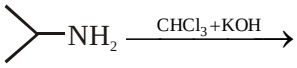
CA0055

(d) 

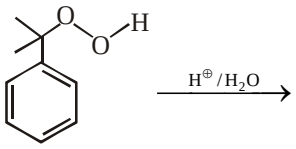
CA0056

(e) 

CA0057

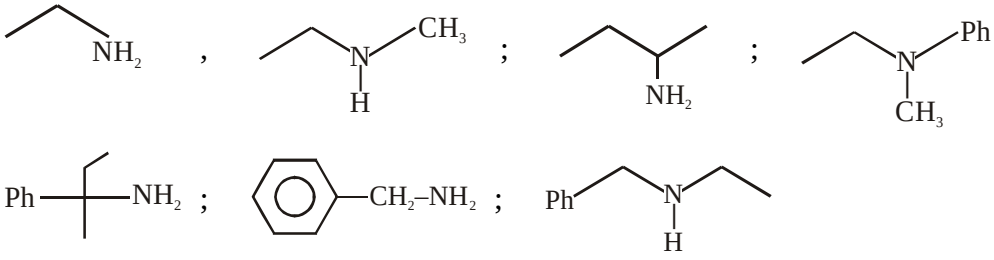
(f) 

CA0058

(g) 

CA0059

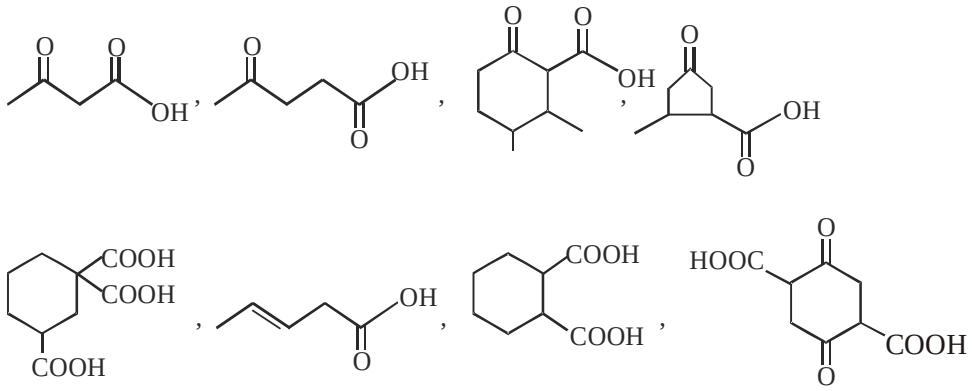
8. Of the following amines how many can be seperated by Hoffmann's mustard oil reaction.



CA0060

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & its Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & its Derivative, Aliphatic Amines (ENG).p65

9. Examine the structure of following compounds, and find out number of compounds that will undergo decarboxylation in presence of heat.



CA0061

10. $CH_3CH_2-\underset{\underset{NH_2}{|}}{CH}-COOH \xrightarrow{\Delta}$ P (no. of products)

$CH_3CH_2-\underset{\underset{OH}{|}}{CH}-COOH \xrightarrow{\Delta}$ Q (no. of products)

$CH_3\underset{\underset{OH}{|}}{CH}-CH_2-COOH \xrightarrow{\Delta}$ R (no. of products)

$\underset{\underset{OH}{|}}{CH_2}-CH_2-CH_2-COOH \xrightarrow{\Delta}$ S (no. of products)

In all reactions the sum of product is.

CA0062

How will you bring about the following transformation:

11. Propanoic acid into lactic acid.

CA0063

12. Ethyl benzene to 2-phenyl propionic acid.

CA0064

13. Acetamide from acetone.

CA0065

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & It's Derivative, Aliphatic Amines (ENG).p65

EXERCISE # (JEE-MAIN)

1. Reaction - **[AIEEE-2002]**

Primary amine + $CHCl_3$ + KOH $\rightarrow$ product, here product will be -

(1) Cyanide (2) Isocyanide (3) Amine (4) Alcohol

CA0066

2. The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is- **[AIEEE-2004]**

(1) $Fe_4[Fe(CN)_6]_3$ (2) $Na_3[Fe(CN)_6]$ (3) $Fe(CN)_3$ (4) $Na_4[Fe(CN)_5)NOS]$

CA0067

3. Which one of the following methods is neither meant for the synthesis nor for separation of amines-

(1) Hofmann method (2) Hinsberg method **[AIEEE-2005]**

(3) Curtius reaction (4) Wurtz reaction

CA0068

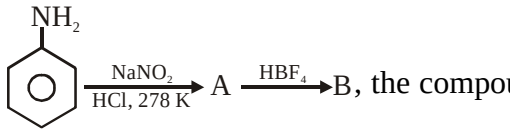
4. In the chemical reaction, $CH_3CH_2NH_2 + CHCl_3 + 3KOH \rightarrow$ (A) + (B) + $3H_2O$, the compounds (A) and (B) are respectively - **[AIEEE-2007]**

(1) C_2H_5CN and 3KCl (2) CH_3CH_2 $CONH_2$ and 3KCl

(3) C_2H_5NC and K_2CO_3 (4) C_2H_5NC and 3KCl

CA0069

5. In the chemical reactions, **[AIEEE-2010]**



, the compounds 'A' and 'B' respectively are :-

(1) Nitrobenzene and chlorobenzene

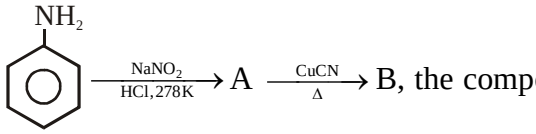
(2) Nitrobenzene and fluorobenzene

(3) Phenol and benzene

(4) Benzene diazonium chloride and fluorobenzene

CA0070

6. In the chemical reactions



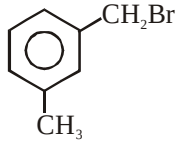
, the compounds A and B respectively are : **[AIEEE-2011]**

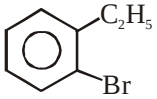
(1) Fluorobenzene and phenol (2) Benzene diazonium chloride and benzonitrile

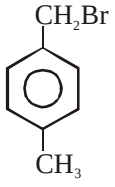
(3) Nitrobenzene and chlorobenzene (4) Phenol and bromobenzene

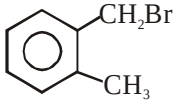
CA0071

7. 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): **[AIEEE-2013]**

(1) 

(2) 

(3) 

(4) 

CA0072

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & its Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & its Derivative, Aliphatic Amines (ENG).p65

8. 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 give $CH_3CH_2NH_2$. A is :- **[AIEEE-2013]**

(1) CH_3COOH (2) $CH_3CH_2CH_2COOH$ (3) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$ (4) CH_3CH_2COOH

CA0073

9. On heating an aliphatic primary amine with chloroform & ethenolic potassium hydroside the organic compound formed is **[AIEEE-2014]**

(1) An alkyl cyanide (2) An alkyl isocyanide

(3) an alkanol (4) an alkanediol

CA0074

10. In the reaction $CH_3COOH \xrightarrow{LiAlH_4} A \xrightarrow{PCl_5} B \xrightarrow{alc.KOH} C$ 'C' is **[AIEEE-2014]**

(1) Ethylene (2) Acetyl chloride (3) Acetaldehyde (4) Acetylene.

CA0075

11. In the presence of a small amount of phosphorous, aliphatic carboxylic acids react with chlorine or bromine to yield a compound in which α - hydrogen has been replaced by halogen. This reaction is known as : **[JEE(Main)-2015]**

(1) Etard reaction (2) Hell - Volhard - Zelinsky reaction

(3) Wolff - Kischner reaction (4) Rosenmund reaction

CA0076

12. In the Hofmann bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are : **[JEE(Main)-2016]**

(1) Four moles of NaOH and one mole of Br_2

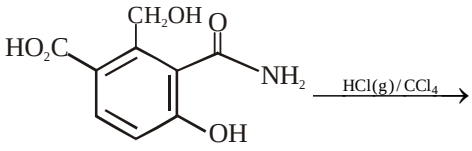
(2) One mole of NaOH and one mole of Br_2

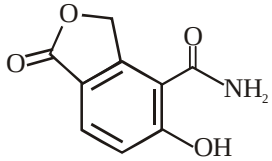
(3) Four moles of NaOH and two moles of Br_2

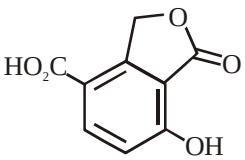
(4) Two moles of NaOH and two moles of Br_2

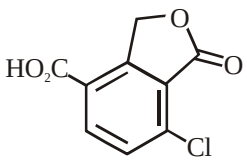
CA0077

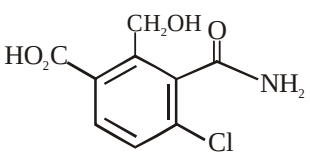
13. The major product expected from the following reaction is : **[JEE(Main On-Line)-2017]**



(1) 

(2) 

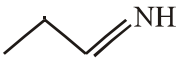
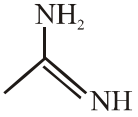
(3) 

(4) 

CA0078

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & It's Derivative, Aliphatic Amines (ENG).p65

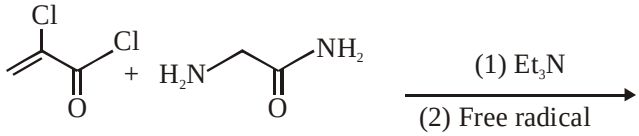
14. The increasing order of basicity of the following compounds is : **[JEE(Main)-2018]**

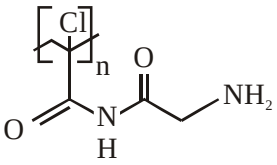
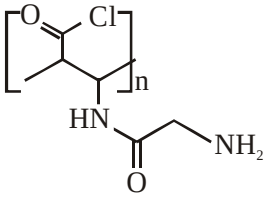
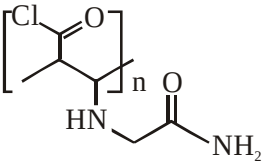
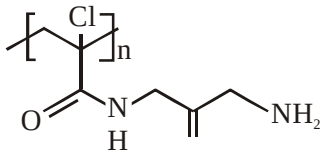
(a)  (b)  (c)  (d) 

(1) (b) < (a) < (c) < (d)
(2) (b) < (a) < (d) < (c)
(3) (d) < (b) < (a) < (c)
(4) (a) < (b) < (c) < (d)

CA0079

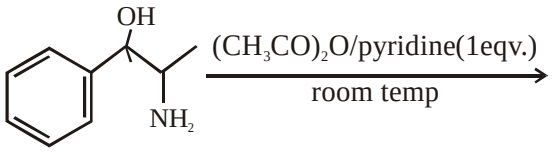
15. Major product of the following reaction is : **[JEE Main (Jan)-2019]**

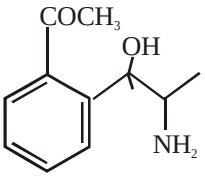
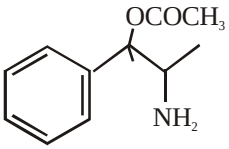
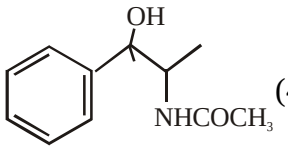
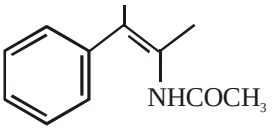


(1) 
(2) 
(3) 
(4) 

CA0080

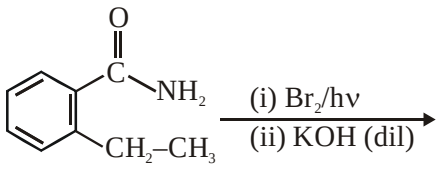
16. The major product obtained in the following reaction is : **[JEE Main (Jan)-2019]**

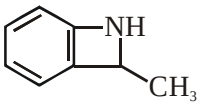
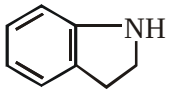
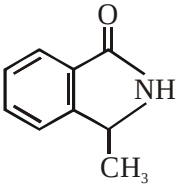
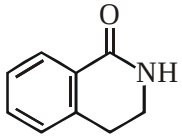


(1) 
(2) 
(3) 
(4) 

CA0081

17. The major product of the following reaction is : **[JEE Main (Jan)-2019]**



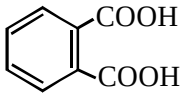
(1) 
(2) 
(3) 
(4) 

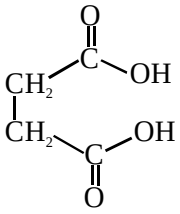
CA0082

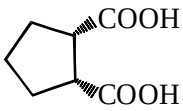
node06\B0BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & its Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & its Derivative, Aliphatic Amines (ENG).p65

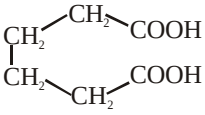
18. Which dicarboxylic acid in presence of a dehydrating agent is least reactive to give an anhydride :

[JEE Main (Jan)-2019]

(1) 

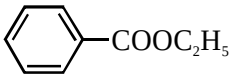
(2) 

(3) 

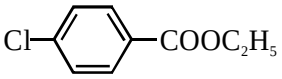
(4) 

CA0083

19. The decreasing order of ease of alkaline hydrolysis for the following esters is :

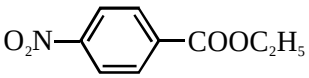


I

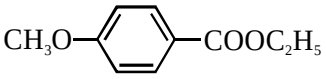


II

[JEE Main (Jan)-2019]



III

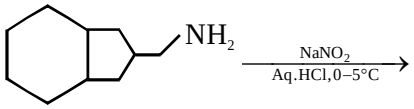


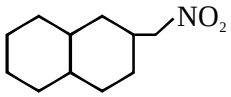
IV

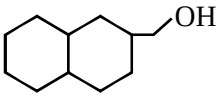
(1) IV > II > III > I (2) III > II > I > IV (3) III > II > IV > I (4) II > III > I > IV

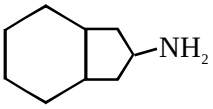
CA0084

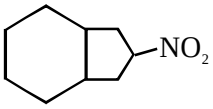
20. The major product formed in the reaction given below will be : **[JEE Main (Jan)-2019]**



(1) 

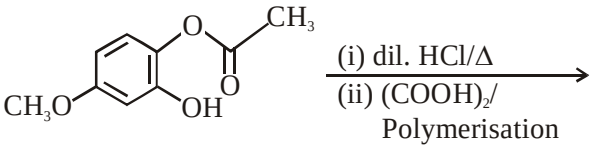
(2) 

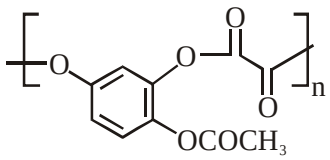
(3) 

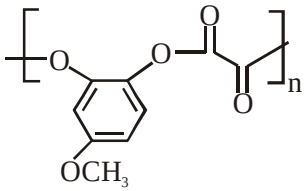
(4) 

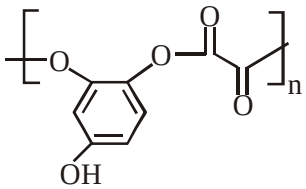
CA0085

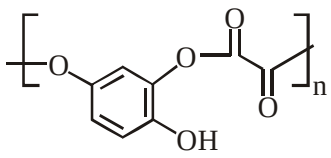
21. The major product of the following reaction is: **[JEE Main (Jan)-2019]**



(1) 

(2) 

(3) 

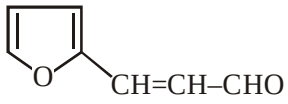
(4) 

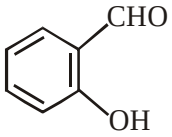
CA0086

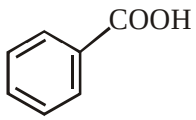
node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & It's Derivative, Aliphatic Amines (ENG).p65

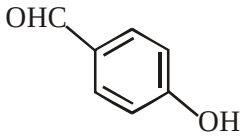
22. An aromatic compound 'A' having molecular formula $C_7H_6O_2$ on treating with aqueous ammonia and heating forms compound 'B'. The compound 'B' on reaction with molecular bromine and potassium hydroxide provides compound 'C' having molecular formula C_6H_7N. The structure of 'A' is :

[JEE Main (Jan)-2019]

(1) 

(2) 

(3) 

(4) 

CA0087

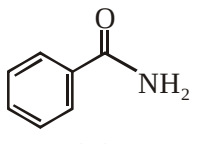
23. A compound 'X' on treatment with Br_2/NaOH, provided C_3H_9N, which gives positive carbylamine test. Compound 'X' is :- **[JEE Main (Jan)-2019]**

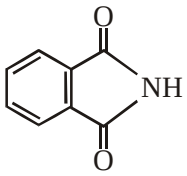
(1) $CH_3COCH_2NHCH_3$ (2) $CH_3CH_2COCH_2NH_2$

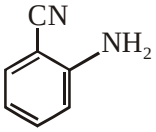
(3) $CH_3CH_2CH_2CONH_2$ (4) $CH_3CON(CH_3)_2$

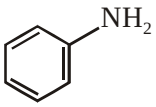
CA0088

24. The increasing order of reactivity of the following compounds towards reaction with alkyl halides directly is : **[JEE Main (Jan)-2019]**


(A)


(B)


(C)

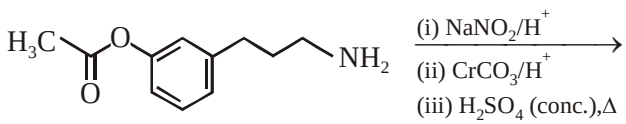

(D)

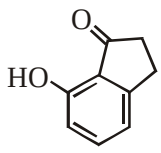
(1) (B) < (A) < (D) < (C) (2) (B) < (A) < (C) < (D)

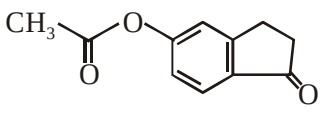
(3) (A) < (C) < (D) < (B) (4) (A) < (B) < (C) < (D)

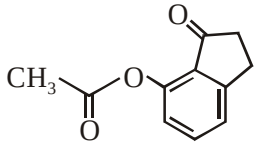
CA0089

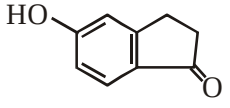
25. The major product of the following reaction is: **[JEE Main (Jan)-2019]**



(1) 

(2) 

(3) 

(4) 

CA0090

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & its Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & its Derivative, Aliphatic Amines (ENG).p65

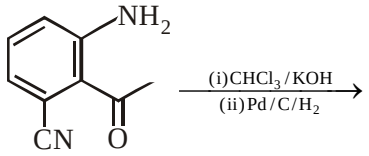
26. Which of the following amines can be prepared by Gabriel phthalimide reaction ?

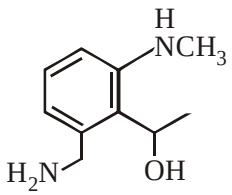
[JEE Main (Apr)-2019]

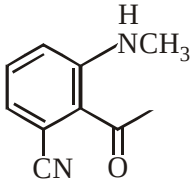
(1) Neo-pentylamine (2) n-butylamine (3) triethylamine (4) t-butylamine

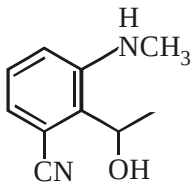
CA0091

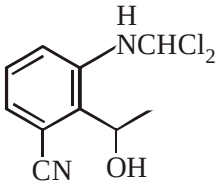
27. The major product obtained in the following reaction is : **[JEE Main (Apr)-2019]**



(1) 

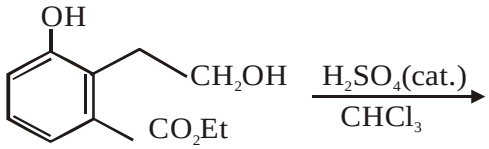
(2) 

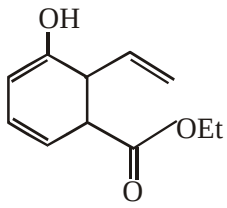
(3) 

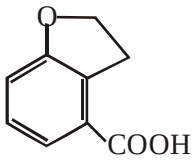
(4) 

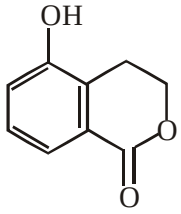
CA0092

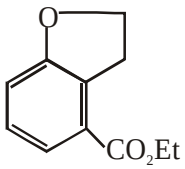
28. The major product of the following reaction is: **[JEE Main (Apr)-2019]**



(1) 

(2) 

(3) 

(4) 

CA0093

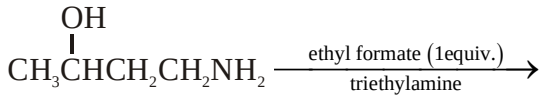
29. Hinsberg's reagent is : **[JEE Main (Apr)-2019]**

(1) $C_6H_5SO_2Cl$ (2) C_6H_5COCl (3) $SOCl_2$ (4) $(COCl)_2$

CA0094

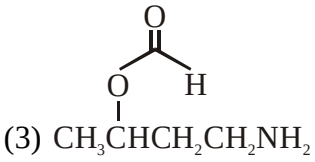
node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & It's Derivative, Aliphatic Amines (ENG).p65

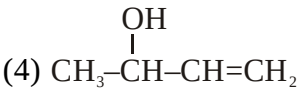
30. The major product of the following reaction is : **[JEE Main (Apr)-2019]**



(1) 

(2)

(3) 

(4) 

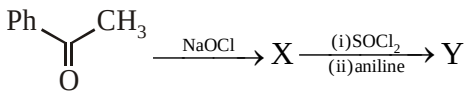
CA0095

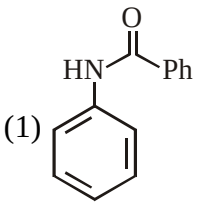
31. Ethylamine ($C_2H_5NH_2$) can be obtained from N-ethylphthalimide on treatment with : **[JEE Main (Apr)-2019]**

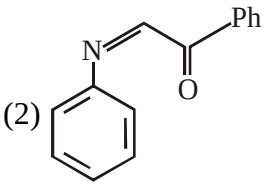
(1) $NaBH_4$ (2) CaH_2 (3) H_2O (4) NH_2NH_2

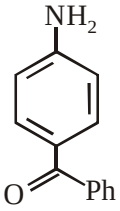
CA0096

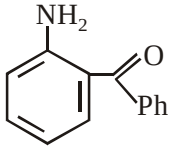
32. The major product 'Y' in the following reaction is:- **[JEE Main (Apr)-2019]**



(1) 

(2) 

(3) 

(4) 

CA0097

node06\B0B0-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & Its Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & Its Derivative, Aliphatic Amines (ENG).p65

EXERCISE # (JEE ADVANCED)

1. Which of the following carboxylic acids undergo decarboxylation easily: **[IIT 1995]**

(A) $C_6H_5CO–CH_2COOH$ (B) $C_6H_5COCOOH$

(C) $C_6H_5\underset{\underset{OH}{|}}{CH_2} - COOH$ (D) $C_6H_5\underset{\underset{NH_2}{|}}{CH_2} - COOH$

CA0098

2. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to : **[IIT 1996]**

(A) Ionization of benzoic acid

(B) Dimerisation of benzoic acid

(C) Trimerisation of benzoic acid

(D) Solvation of benzoic acid

CA0099

3. When propionic acid is treated with aqueous $NaHCO_3$, CO_2 is liberated. The 'C' of CO_2 comes from.

(A) Methyl group (B) Carboxylic acid group

(C) methylene group (D) bicarbonate **[IIT 1999]**

CA0100

4. Benzoyl chloride is prepared from benzoic acid by: **[IIT 2000]**

(A) Cl_2, hν (B) SO_2Cl_2 (C) $SOCl_2$ (D) Cl_2, H_2O

CA0101

5. Which of the following acids has the smallest dissociation constant? **[IIT 2002]**

(A) $CH_3CHFCOOH$ (B) FCH_2CH_2COOH

(C) $BrCH_2CH_2COOH$ (D) $CH_3CHBrCOOH$

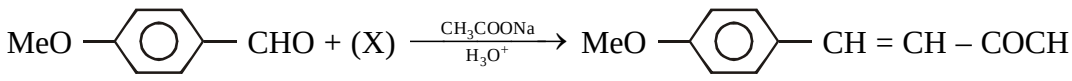
CA0102

6. When benzamide is treated with $POCl_3$, the product is: **[IIT 2004]**

(A) Benzonitrile (B) Aniline (C) Chlorobenzene (D) Benzylamine

CA0103

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & It's Derivative, Aliphatic Amines (ENG).p65

7. 

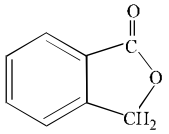
The compound (X) is **[IIT 2005]**

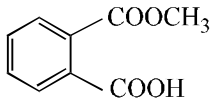
(A) $(CH_3CO)_2O$ (B) Br CH_2 – COOH

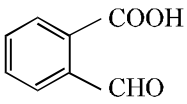
(C) CH_3COOH (D) CHO – COOH

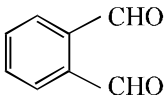
CA0104

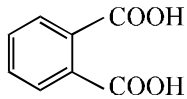
8. Which of the following reactants on reaction with conc. NaOH followed by acidification gives the following lactone as the only product? **[IIT 2006]**



(A) 

(B) 

(C) 

(D) 

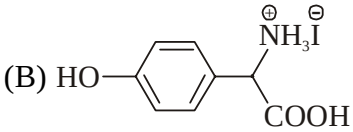
CA0105

9. Match the compounds in **Column I** with their characteristic test(s)/reaction(s) given in **Column II**. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS.

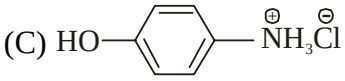
Column-I **Column-II** **[IIT 2008]**

(A) $H_2N - \overset{\oplus}{N}H_3\overset{\ominus}{Cl}$

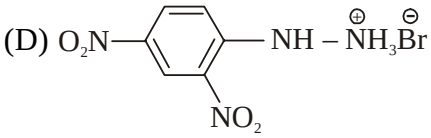
(P) Sodium fusion extract of the compound gives Prussian blue colour with $FeSO_4$

(B) 

(Q) Gives positive $FeCl_3$ test

(C) 

(R) Gives white precipitate with $AgNO_3$

(D) 

(S) Reacts with aldehydes to form the corresponding hydrazone derivative

CA0106

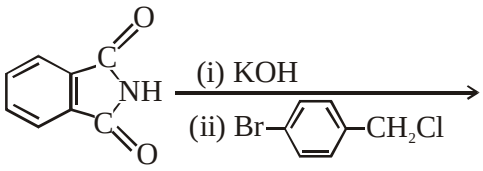
node06\B0B0-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & its Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & its Derivative, Aliphatic Amines (ENG).p65

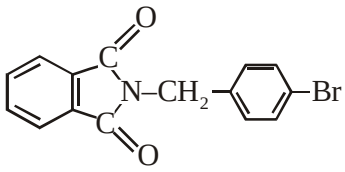
10. Match each of the compound in Column I with its characteristic reaction(s) in Column II.

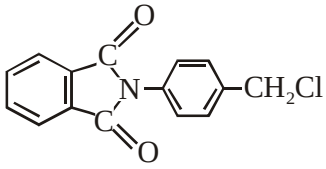
Column-I	**Column-II** **[IIT 2009]**
(A) $CH_3CH_2CH_2CN$	(P) Reduction with Pd–C / H_2
(B) $CH_3CH_2OCOCH_3$	(Q) Reduction with $SnCl_2$ / HCl
(C) $CH_3 - CH = CH - CH_2OH$	(R) Development of foul smell on treatment with chloroform and alcoholic KOH
(D) $CH_3CH_2CH_2CH_2NH_2$	(S) Reduction with diisobutylaluminium hydride (DIBAL-H)
	(T) Alkaline hydrolysis

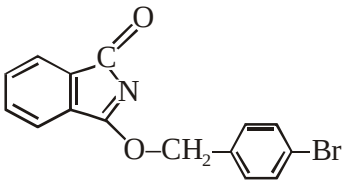
CA0107

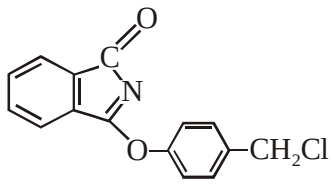
11. The major product of the following reaction is **[IIT 2011]**



(A) 

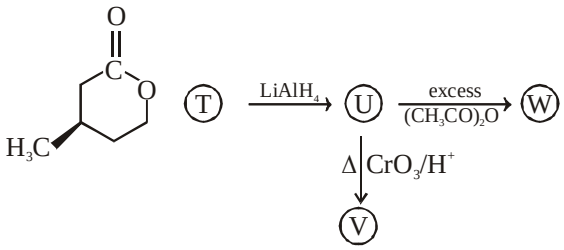
(B) 

(C) 

(D) 

CA0108

12. With reference the scheme given, which of the given statement(s) about T, U, V & W is/are correct **[IIT 2012]**



(A) 'T' is soluble in hot aq NaOH

(B) 'U' is optically active

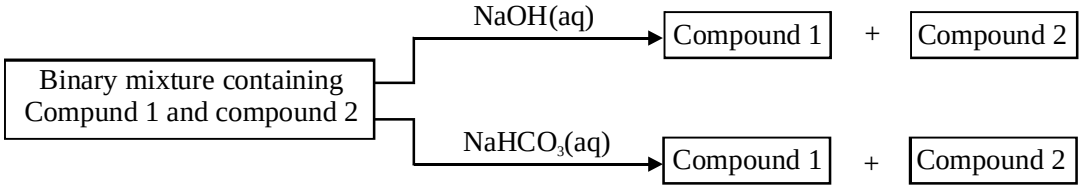
(C) mol formula of W is $C_{10}H_{18}O_4$

(D) V gives effervescence with aq $NaHCO_3$

CA0109

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & It's Derivative, Aliphatic Amines (ENG).p65

13. Identify the binary mixtures (s) that can be separated into the individual compounds, by differential extraction, as shown in the given scheme - **[IIT 2012]**

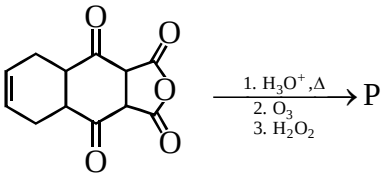


(A) C_6H_5OH and C_6H_5COOH (B) C_6H_5COOH and $C_6H_5CH_2OH$

(C) $C_6H_5CH_2OH$ and C_6H_5OH (D) $C_6H_5CH_2OH$ and $C_6H_5CH_2COOH$

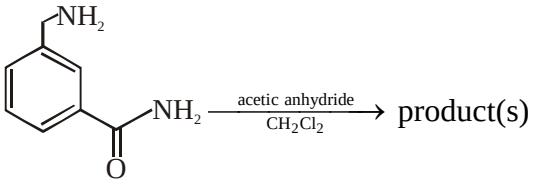
CA0110

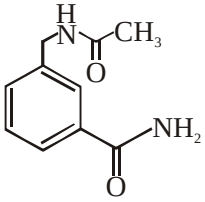
14. The total number of carboxylic acid groups in the product P is **[IIT 2013]**

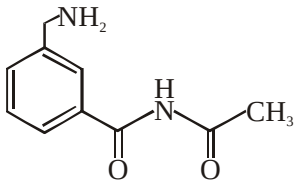


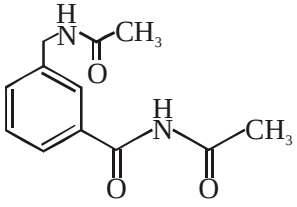
CA0111

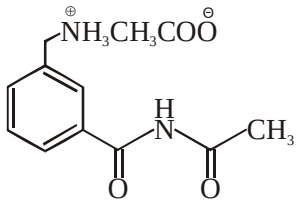
15. In the reaction shown below, the major product(s) formed is / are : **[IIT 2014]**



(A)  + CH_3COOH

(B)  + CH_3COOH

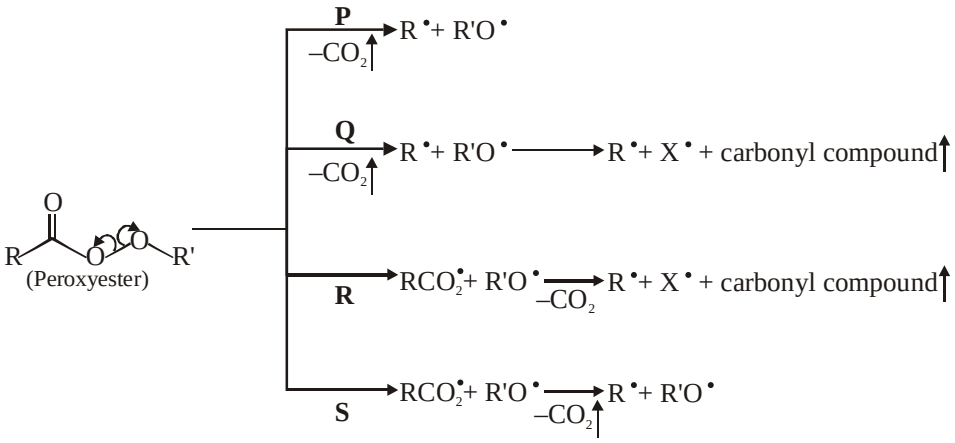
(C)  + H_2O

(D) 

CA0112

node06\B0B0-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & its Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & its Derivative, Aliphatic Amines (ENG).p65

16. Different possible **<u>thermal</u>** 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. **[IIT 2014]**



List-I

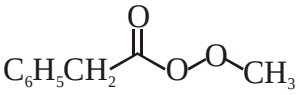
(P) Pathway **P**

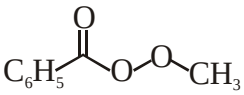
(Q) Pathway **Q**

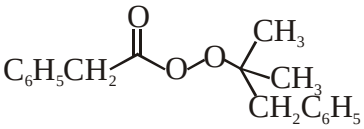
(R) Pathway **R**

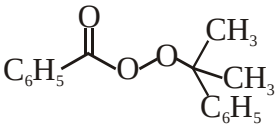
(S) Pathway **S**

List-II

(1) 

(2) 

(3) 

(4) 

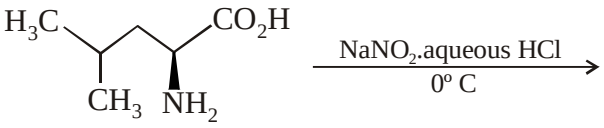
Code :

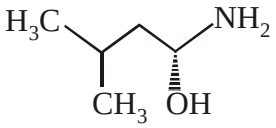
	P	Q	R	S
(A)	1	3	4	2
(B)	2	4	3	1
(C)	4	1	2	3
(D)	3	2	1	4

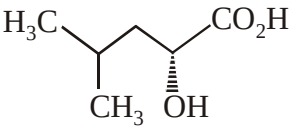
CA0113

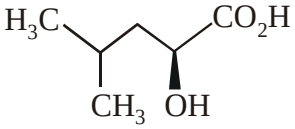
node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & It's Derivative, Aliphatic Amines (ENG).p65

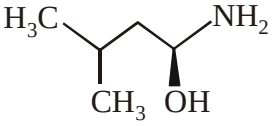
17. The major product of the reaction is : **[IIT 2015]**



(A) 

(B) 

(C) 

(D) 

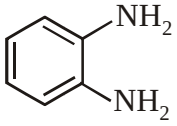
CA0114

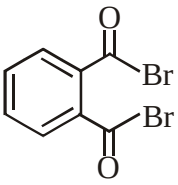
PARAGRAPH FOR NO. 18 & 19

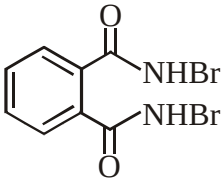
Treatment of compound **O** with $KMnO_4$ / H^+ gave **P**, which on heating with ammonia gave The compound **Q** on treatment with Br_2 / NaOH produced **R**. On strong heating, **Q** gave **S**, which on further treatmenet with ethyl 2-bromopropanoate in the presence of KOH following by acidification, gave a compound **T**. **[IIT-JEE-2016]**

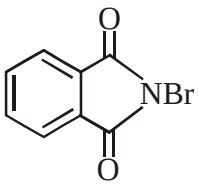
(O)

18. The compound **R** is :

(A) 

(B) 

(C) 

(D) 

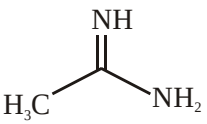
CA0115

19. The compound **T** is :

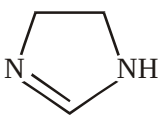
(A) Glycine (B) Alanine (C) Valine (D) Serine

CA0116

20. The order of basicity among the following compounds is **[IIT-JEE(Adv.)-2017]**

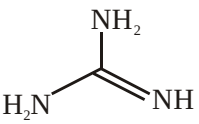


I



II

III



IV

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

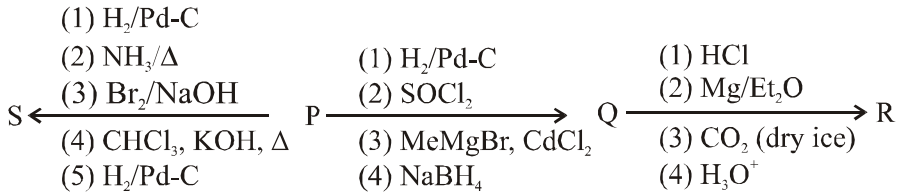
(C) I > IV > III > II (D) IV > I > II > III

CA0117

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & its Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & its Derivative, Aliphatic Amines (ENG).p65

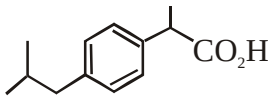
PARAGRAPH FOR NO. 21 & 22

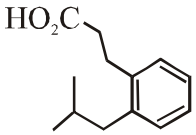
An organic acid P ($C_{11}H_{12}O_2$) can easily be oxidized to a dibasic acid which reacts with ethyleneglycol to produce a polymer dacron. Upon ozonolysis, **P** gives an aliphatic ketone as one of the products. **P** undergoes the following reaction sequences to furnish **R** via The compound **P** also undergoes another set of reactions to produce **S.** **[IIT-JEE(Adv.)-2018]**

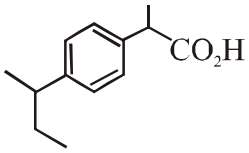


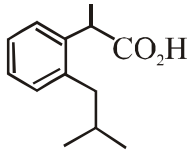
(There are two questions based on PARAGRAPH "A", the question given below is one of them)

21. The compound **R** is

(A) 

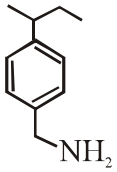
(B) 

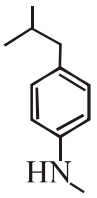
(C) 

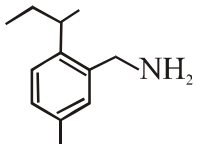
(D) 

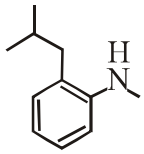
CA0118

22. The compound **S** is

(A) 

(B) 

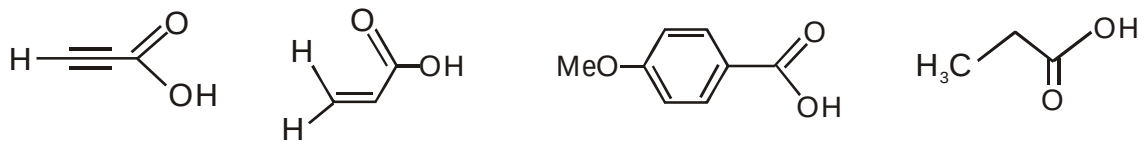
(C) 

(D) 

CA0119

23. The correct order of acid strength of the following carboxylic acids is -

[IIT-JEE(Adv.)-2019]



I II III IV

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

CA0120

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & It's Derivative, Aliphatic Amines (ENG).p65

ANSWER KEY

EXERCISE # O-I

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

EXERCISE # O-II

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

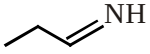
EXERCISE # S-I

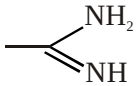
1	**Ans. (A)→P, S ; (B)→Q, S ; (C)→P, S ; (D)→R**						
2	**Ans. (A)→S ; (B)→R ; (C)→P ; (D)→Q**	3	**Ans. (A)→S ; (B)→R ; (C)→P ; (D)→Q**				
4	**Ans. (A)→R ; (B)→S ; (C)→Q ; (D)→P**	5	**Ans. (A)→P ; (B)→Q ; (C)→S ; (D)→R, S**				
6	**Ans. (A)→P ; (B)→R ; (C)→P, S ; (D)→Q**						
7	**Ans. (4)**	8	**Ans. (4)**	9	**Ans. (5)**	10	**Ans. (9)**

EXERCISE # (JEE-MAIN)

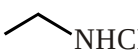
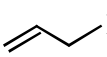
1	**Ans. (2)**	2	**Ans. (1)**	3	**Ans. (4)**	4	**Ans. (4)**
5	**Ans. (4)**	6	**Ans. (2)**	7	**Ans. (4)**	8	**Ans. (4)**
9	**Ans. (2)**	10	**Ans. (1)**	11	**Ans. (2)**	12	**Ans. (1)**
13	**Ans. (1)**						
14	**Ans. (2)**						

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

In compound  nitrogen is sp^2 hybridized so least basic among all given compound.

compound  is very strong nitrogeneous organic base as lone pair of one nitrogen delocalize in resonance and make another nitrogen negativly charged and conjugate acid have two equivalent resonating structure.

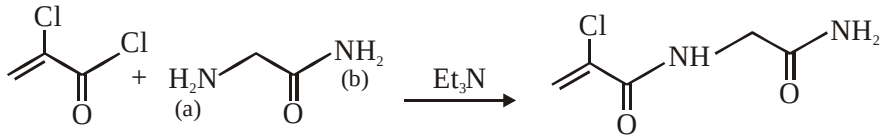
Thus it is most basic in given compouds.

 (secondary amine) more basic than  (primary amine)

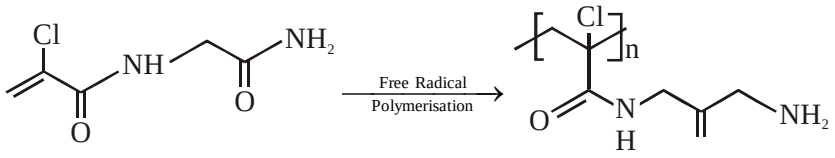
node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & Its Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & Its Derivative, Aliphatic Amines (ENG).p65

15. Ans. (4)

Sol.

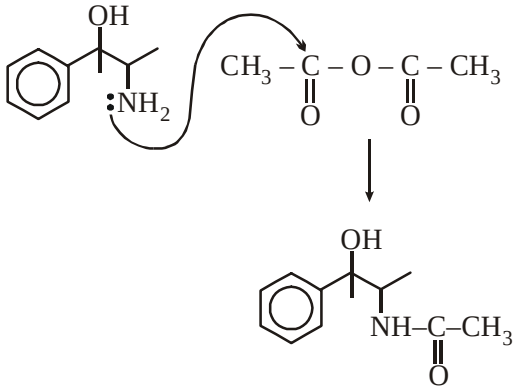


NH_2(a) will wact as nucleophile as (b) is having delocalised lonepair.



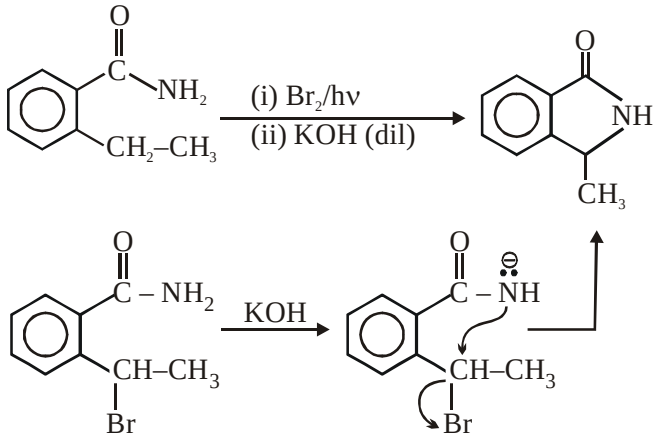
16. Ans. (3)

Sol.



17. Ans. (3)

Sol.



18. Ans. (4)

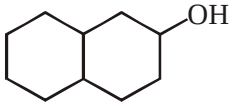
Sol. Adipic acid $CO_2H–(CH_2)_4–CO_2H \xrightarrow[\text{agent}]{\text{dehydrating}}$ 7 membered cyclic anhydride (Very unstable)

19. Ans. (2)

Sol. More is the electrophilic character of carbonyl group of ester faster is the alkaline hydrolysis.

20. Ans. (Bonus)

Sol. Answer should be



21. Ans. (2)

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & It's Derivative, Aliphatic Amines (ENG).p65

22. Ans. (3)

23. Ans. (3)

Sol.

$$[X] \xrightarrow[NaOH]{Br_2} C_3H_9N \xrightarrow[KOH]{CHCl_3} CH_3CH_2CH_2\text{–}NC$$

Hoff mann's Bromaide degradation

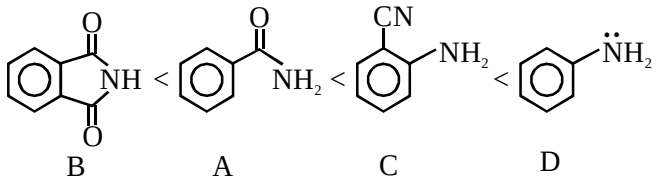
Carbylamine Reaction

Thus [X] must be aride with oen carbon more than is amine.

Thus [X] is $CH_3CH_2CH_2CONH_2$

24. Ans. (2)

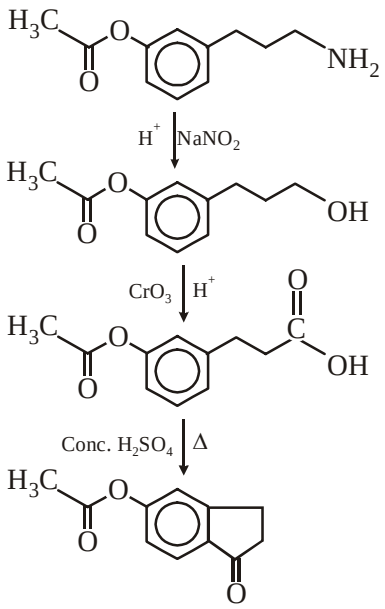
Sol. Nucleophilicity order



B A C D

25. Ans. (4)

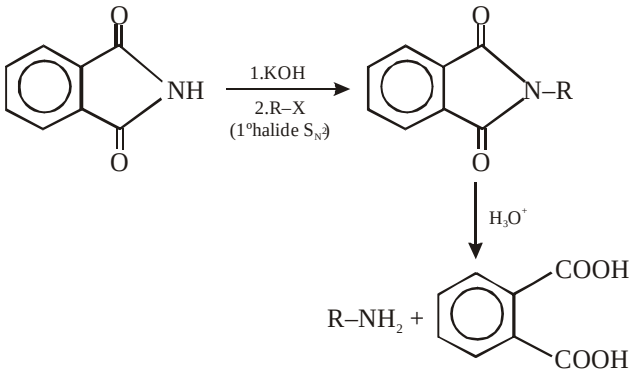
Sol.



26. Ans. (2)

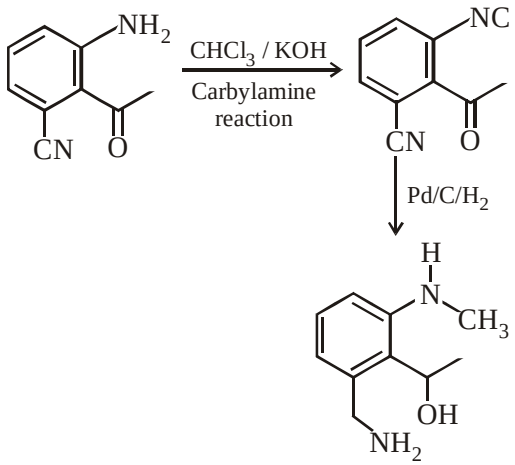
Sol. Gabriel phthalimide synthesis :

node06\B0B0-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & its Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & its Derivative, Aliphatic Amines (ENG).p65



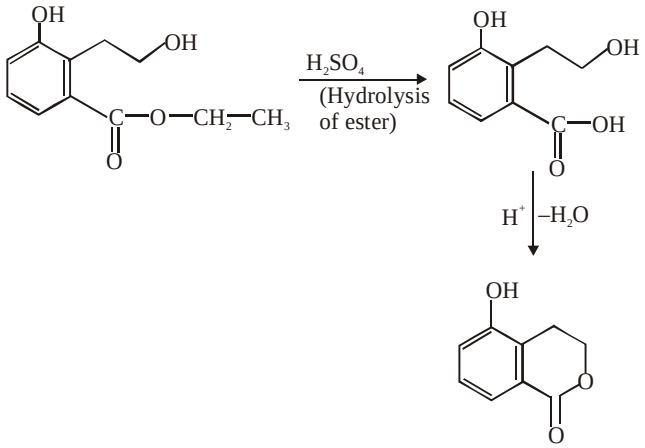
27. Ans. (1)

Sol.



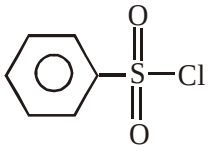
28. Ans. (3)

Sol.



29. Ans.(1)

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & It's Derivative, Aliphatic Amines (ENG).p65

Sol. Hinsberg Reagenl $\Rightarrow$ 

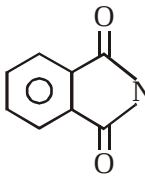
[Benzene Sulphonyl chloride]

30. Ans. (1)

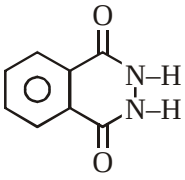
Sol. $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_2-NH_2 \xrightarrow[\text{triethylamine}]{\text{ethyl formate (1equiv.)}} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_2-NH-\underset{\displaystyle O}{\overset{\|}{C}}-H$

as NH_2 is a better nucleophile than OH.

31. Ans. (4)

Sol.  $\xrightarrow{H_2N-NH_2}$ $C_2H_5NH_2$

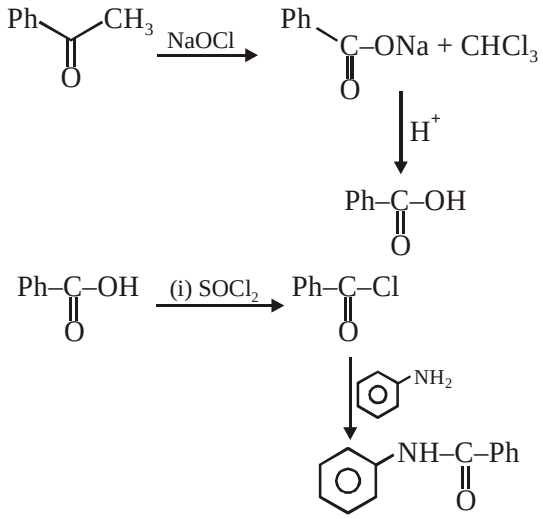
reagent is NH_2-NH_2 byproduct will be



32. Ans. (1)

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & Its Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & Its Derivative, Aliphatic Amines (ENG).p65

Sol.



EXERCISE # (JEE ADVANCED)

1 **Ans. (A)** 2 **Ans. (B)** 3 **Ans. (D)**

4 **Ans. (C)** 5 **Ans. (C)** 6 **Ans. (A)** 7 **Ans. (A)**

8 **Ans. (C)** 9 **Ans. (A)→R, S ; (B)→P, Q ; (C)→P, Q, R ; (D)→P,S**

10 **Ans. (A)→P, Q, S, T ; (B)→P, S, T ; (C)→P ; (D)→R** 11 **Ans. (A)**

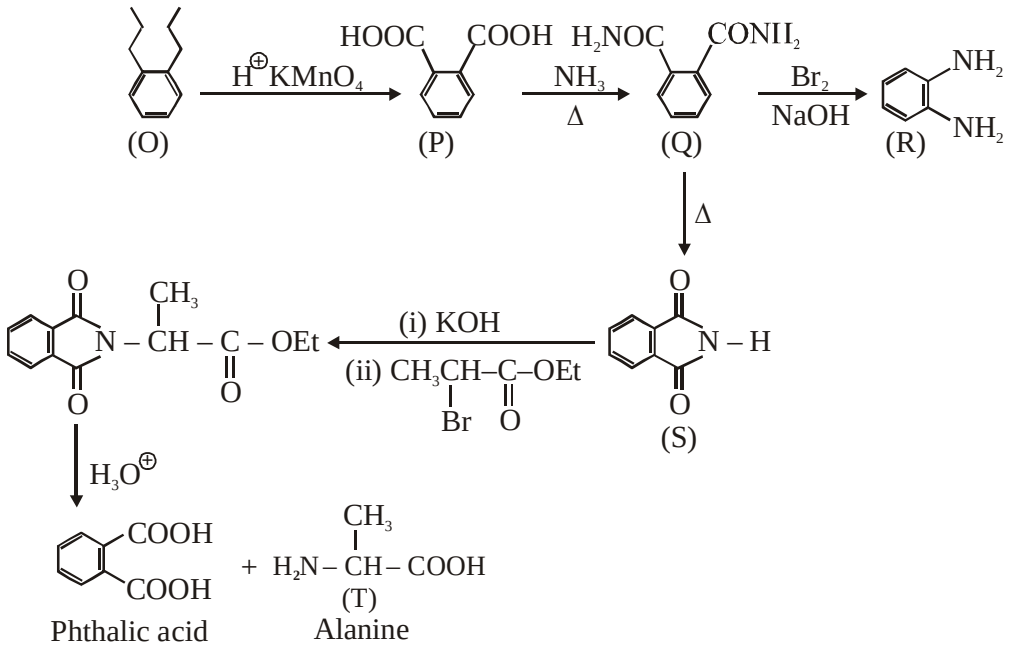
12 **Ans. (A,C,D)** 13 **Ans. (B,D)** 14 **Ans. (2)** 15 **Ans. (A)**

16 **Ans. (A)** 17 **Ans. (C)**

18. Ans. (A)

19. Ans. (B)

Solution 18 & 19.



node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & It's Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & It's Derivative, Aliphatic Amines (ENG).p65

Q to R is Hoffmann's bromamide degradation reaction

S to T is Gabriel's phthalimide sysnthesis

20. Ans. (D) IV > I > II > III

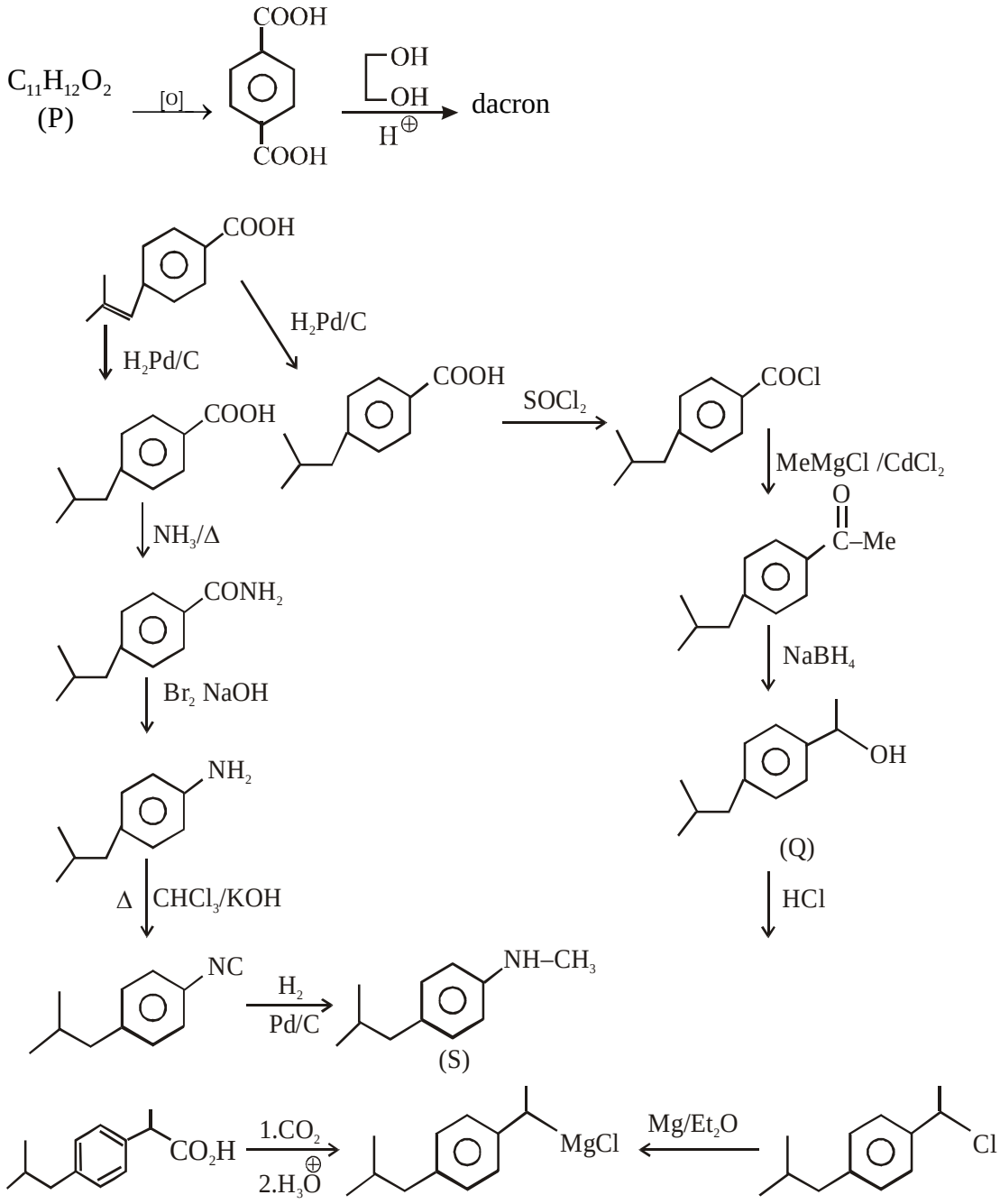
Sol. Basic strength $\propto$ stability of conjugated acid.

$\propto$ + M / +H / +I

21. Ans. (A)

22. Ans. (B)

Solution 21 & 22.



23. Ans. (D)

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Carboxylic Acid & its Derivative, Aliphatic Amines\Eng\02_Carboxylic Acid & its Derivative, Aliphatic Amines (ENG).p65