B Sc SEM IV Chemistry (Hons): CORE IX
Organic Chemistry

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B C College, Asansol
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Unit-III: Amino Acids

Essential and non-essential amino acids, isoelectric point, ninhydrin reaction, synthesis of glycine, alanine and tryptophan; classification of proteins, geometry of peptide linkage

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Amino acids

The amino acids contain at least one amino roup (-NH_2) and one acidic functional group. The acidic functional group may be either –COOH or –SO_3H

Proteins are bio-polymer of amino acids. When protein are hydrolysed by acids, alkalis or enzymes, a mixture of amino acids is obtained.

Classification

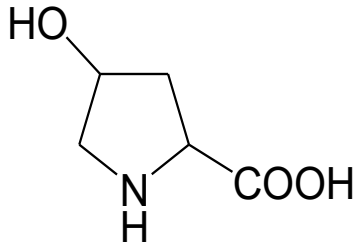
On the basis of source

1. Protein amino acids 2. Non-Protein amino acids (Example: Sarcosin, Ornithine etc)

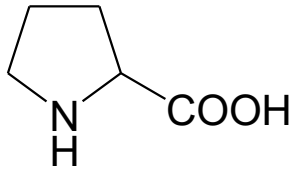
No. Of protein amino acids are 20+2=22

Except 2 all amino acids are α-Amino acids

Proline and Hydroxy Proline are two imino amino acids



Hydroxy-Proline



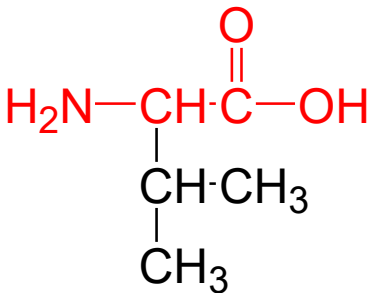
Proline

On the basis of Growth

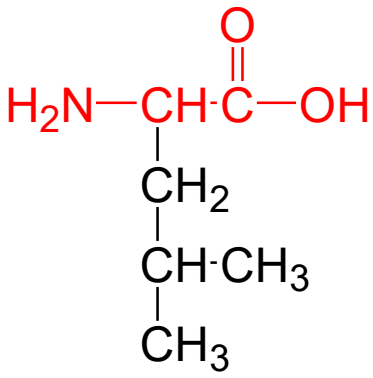
1. Essential amino acids 2. Non-essential amino acids

Essential amino acids

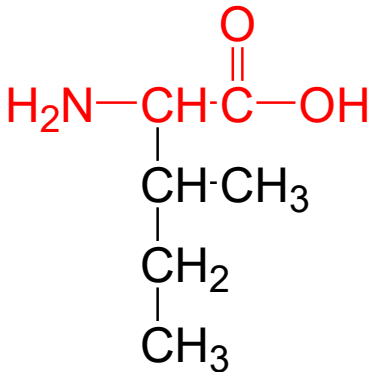
Those amino acids which can not be synthesised by higher animals, specially human body, are called essential amino acids.



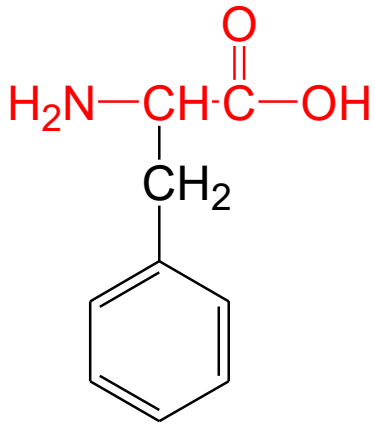
Valine (Val; pI-6.0)



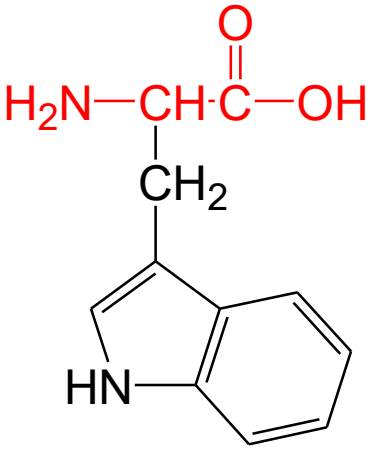
Leucine (Leu; pI-6.0)



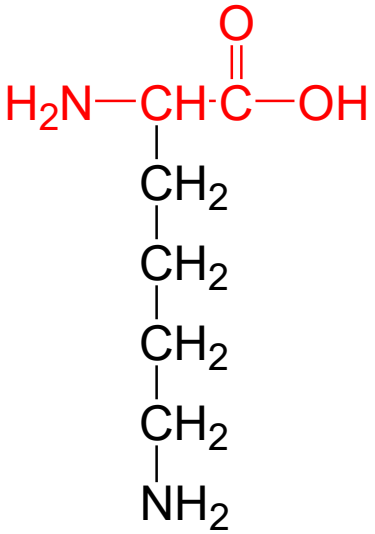
Isoleucine (Ile; pI-6.1)



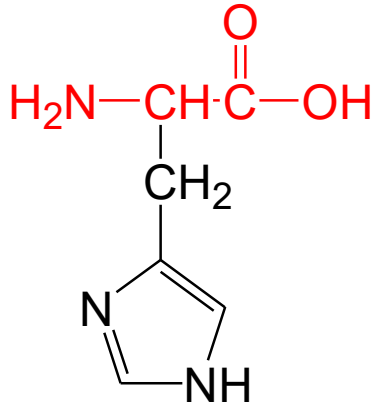
Phenylalanine (Phe; pI-5.5)



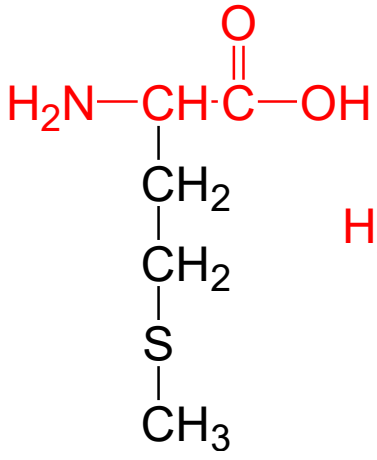
Tryptophan (Trp; pI-5.9)



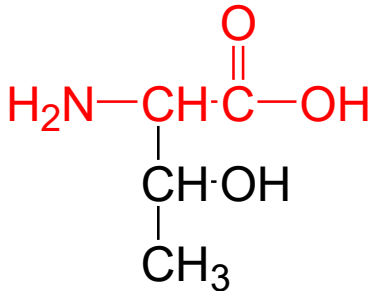
Lysine (Lys; pI-9.8)



Histidine (His; pI-7.6)



Methionine (Met; pI-5.8)

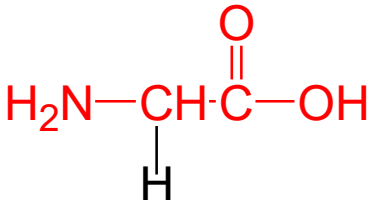


Threonine (Thr; pI-6.5)

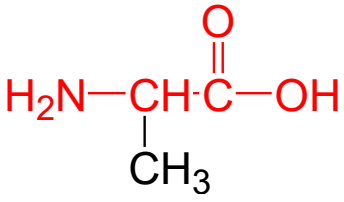
Non-Essential amino acids

Those amino acids which can be synthesised by human body, are called Non-essential amino acids.

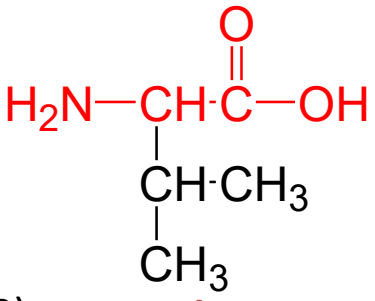
Neutral Amino acids



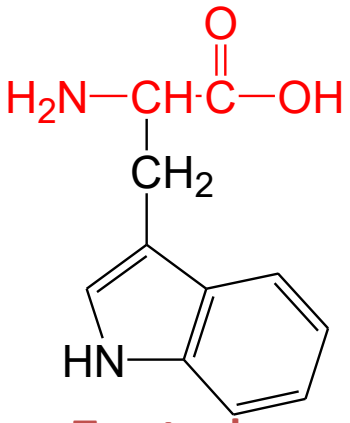
Glycine (Gly; pI-6.0)



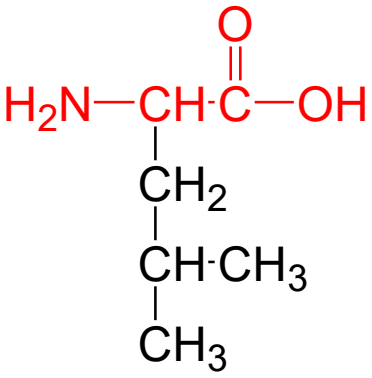
Alanine (Ala; pI-6.0)



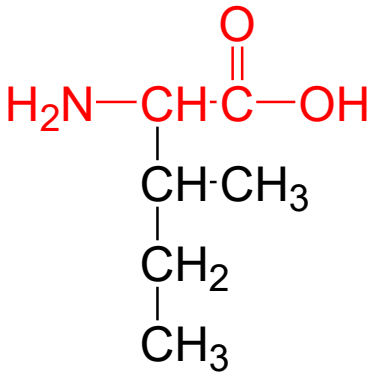
Valine (Val; pI-6.0)



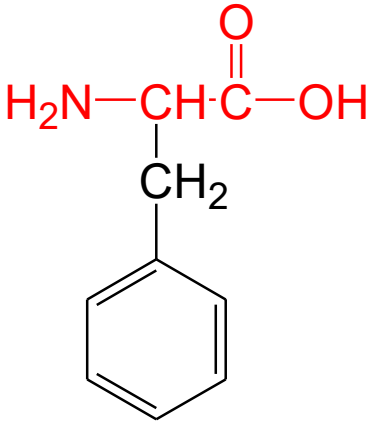
Tryptophan (Trp; pI-5.9)



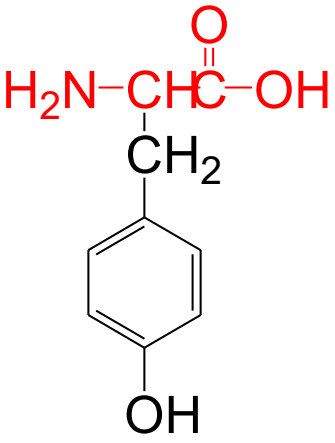
Leucine (Leu; pI-6.0)



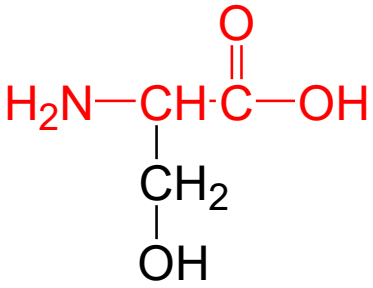
Isoleucine (Ile; pI-6.1)



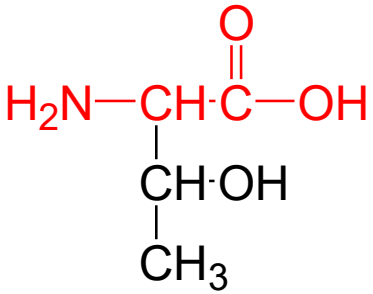
Phenylalanine (Phe; pI-5.5)



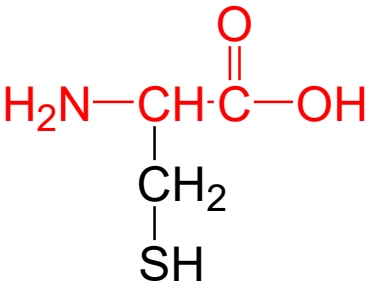
Tyrosine (Tyr; pI-5.7)



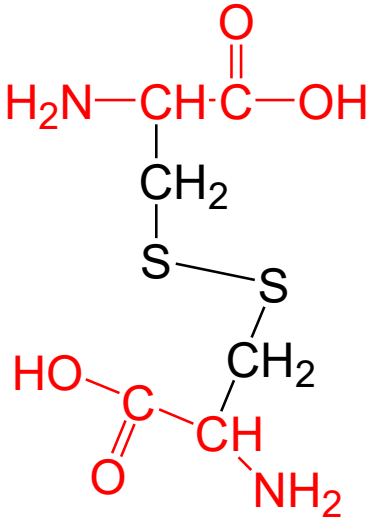
Serine
(Ser; pI-5.7)



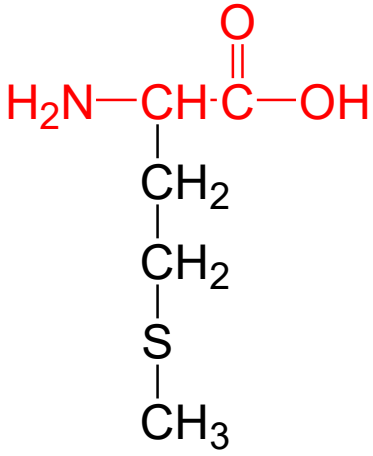
Threonine
(Thr; pI-6.5)



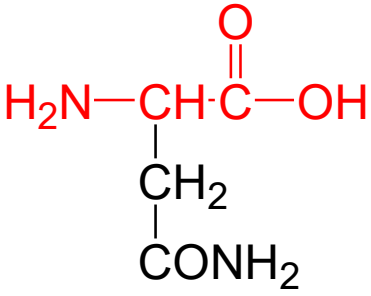
Cysteine
(Cys; pI-5.0)



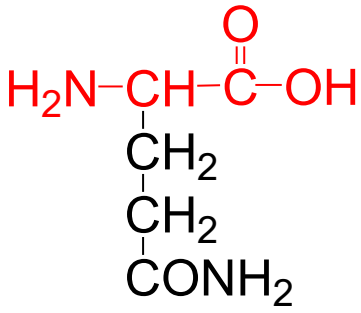
Cystine
(Cys-Cys; pI-5.1)



Methionine
(Met; pI-5.8)

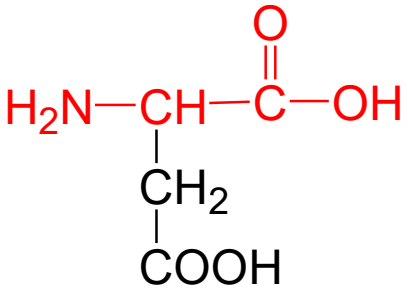


Asparagine
(Asn; pI-5.4)

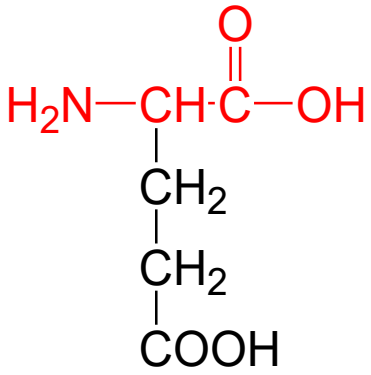


Glutamine
(Gln; pI-5.7)

Acidic Amino acids

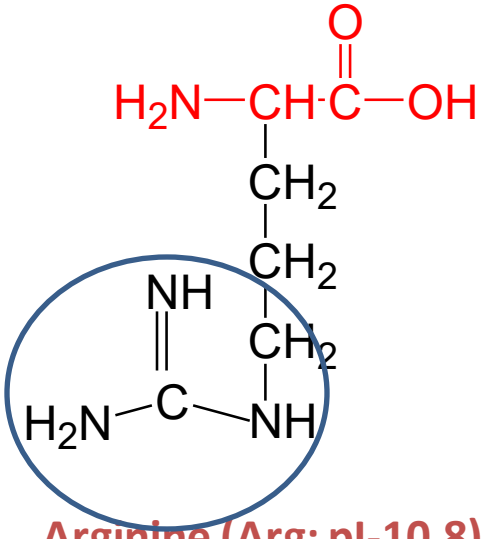


Aspartic Acid (Asp; pI-3.0)

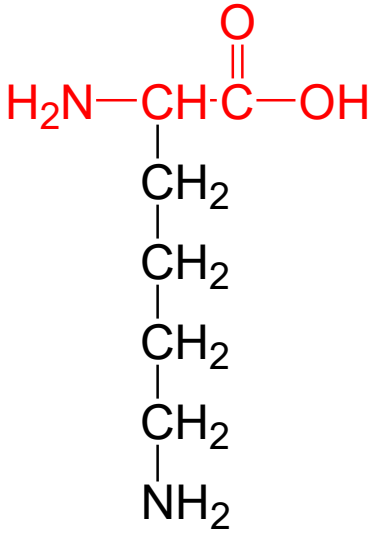


Glutamic Acid (Glu; pI-3.2)

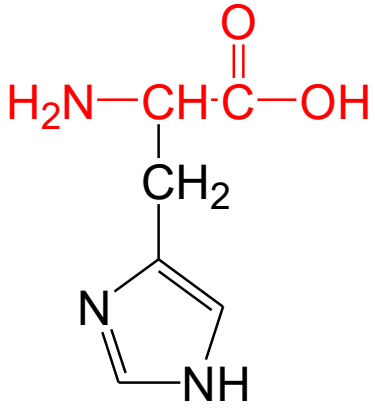
Basic Amino acids



Arginine (Arg; pI-10.8)

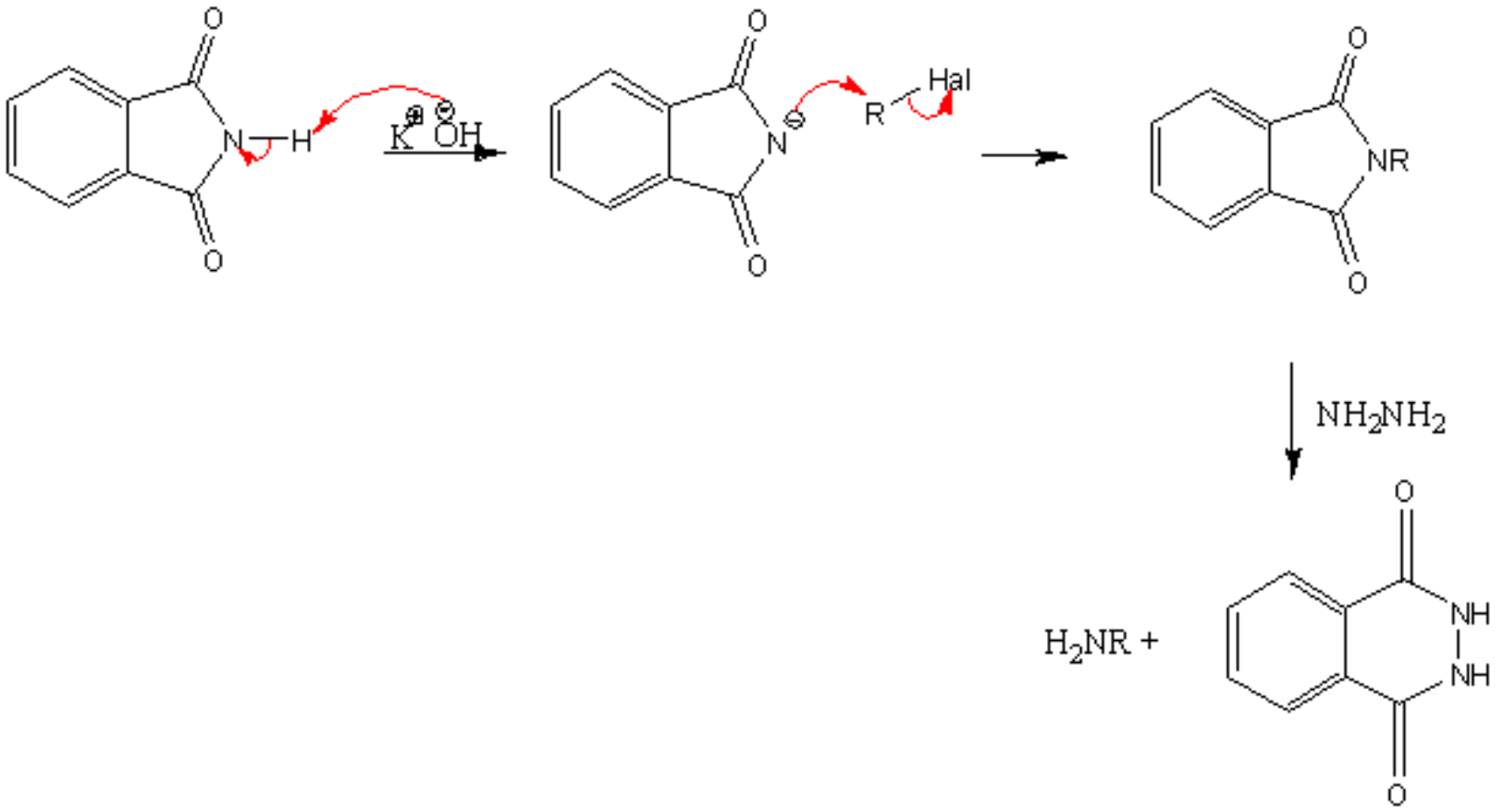


Lysine (Lys; pI-9.8)



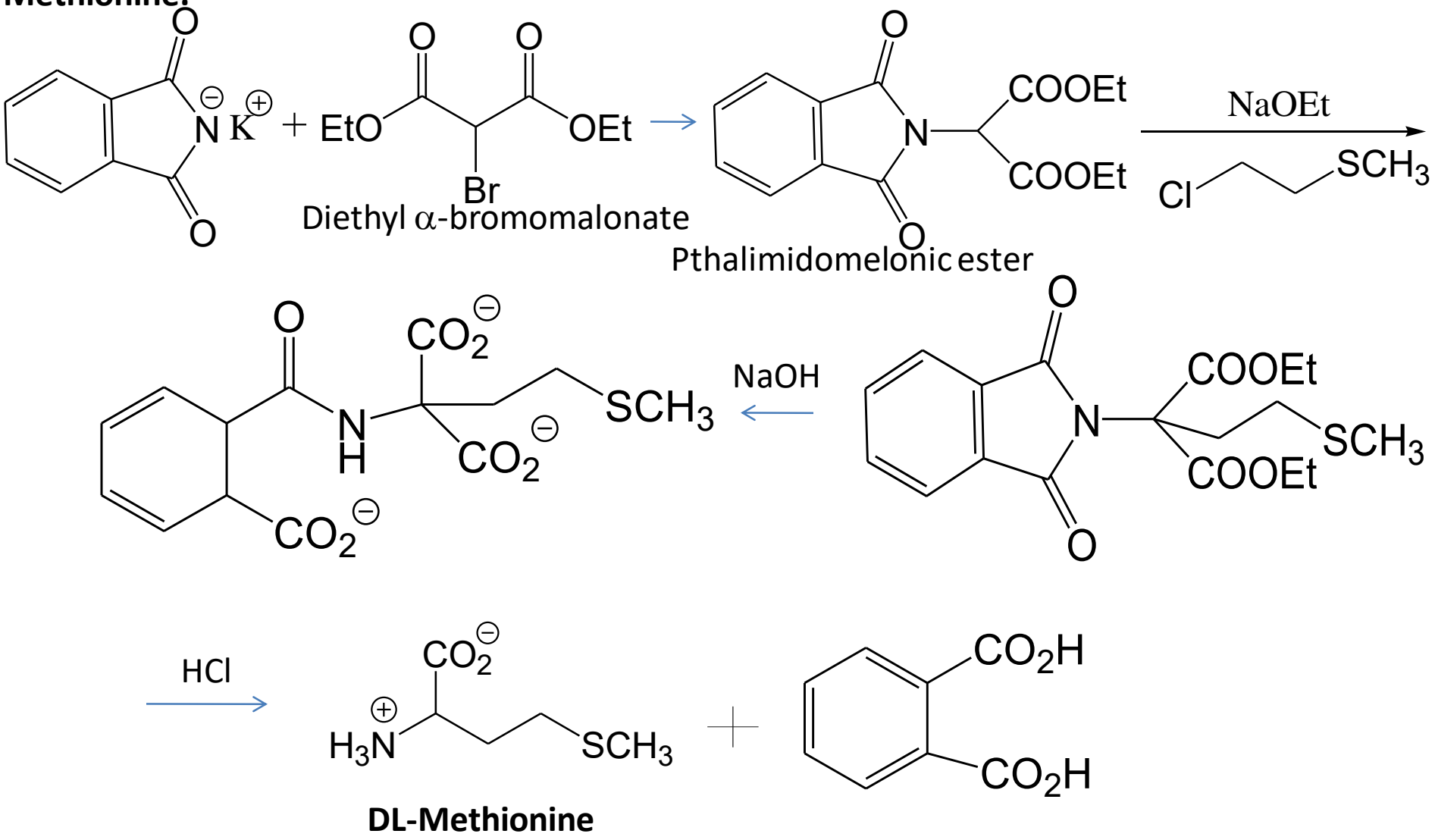
Histidine
(His; pI-7.6)

Gabriel Synthesis for amine:

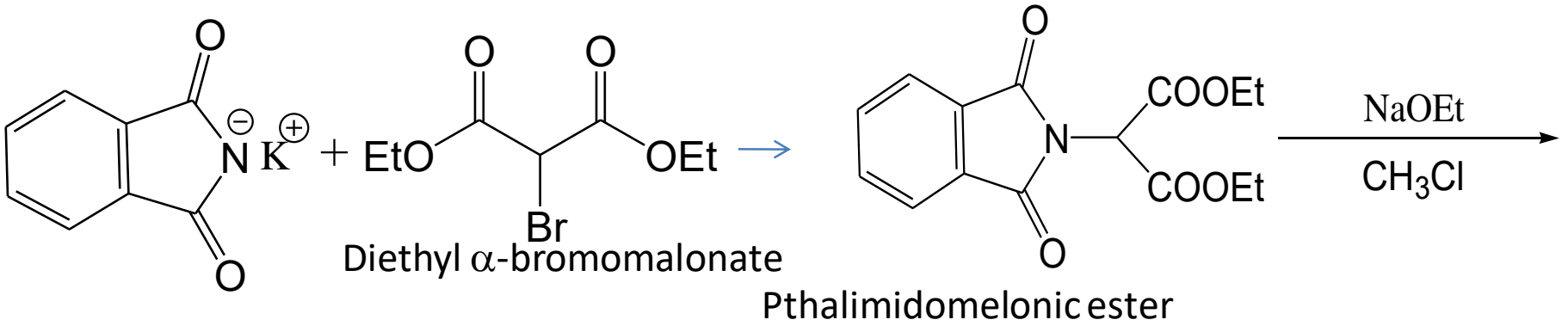


Gabriel Synthesis for Methionine:

This method, a modification of Gabriel synthesis of amines , uses potassiam pthalimide and diethyl –bromomalonate to prepare an imido malonic ester. For example synthesis of **DL-Methionine.**

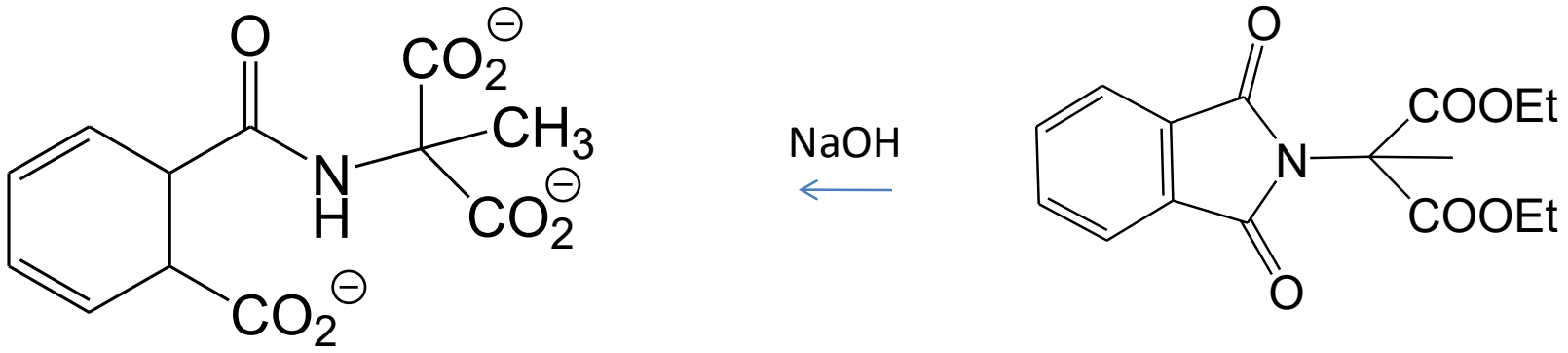


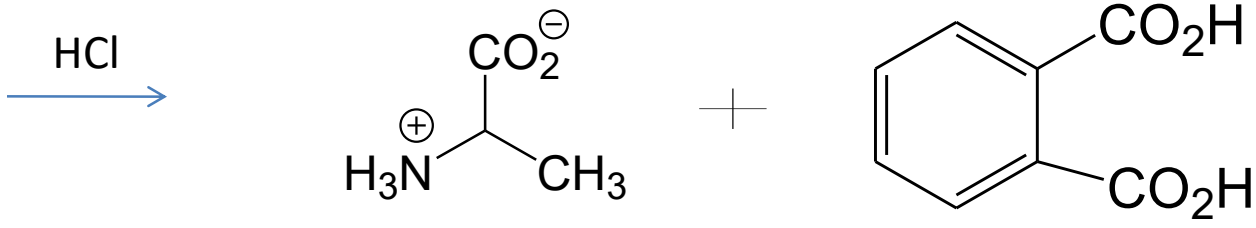
Gabriel Synthesis for Alanine:



Diethyl α-bromomalonate

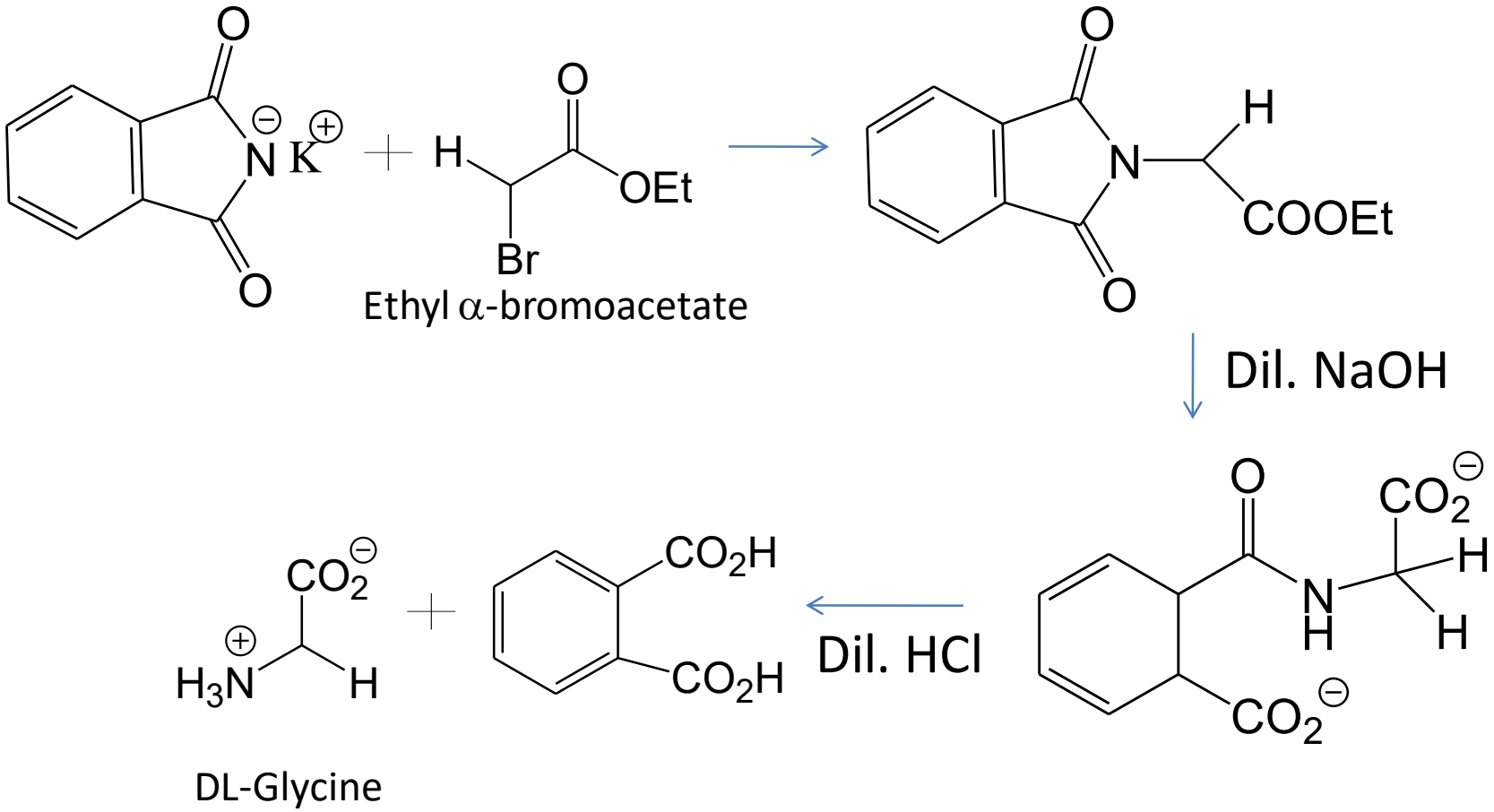
Pthalimidomelonic ester





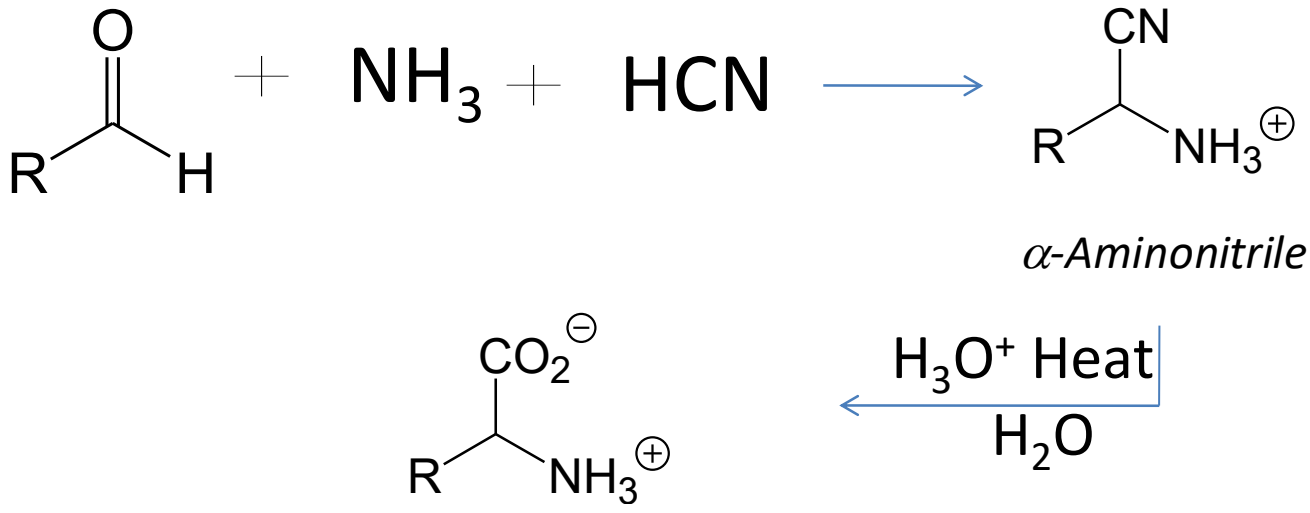
DL-Alanine

Gabriel Synthesis for Glycine:



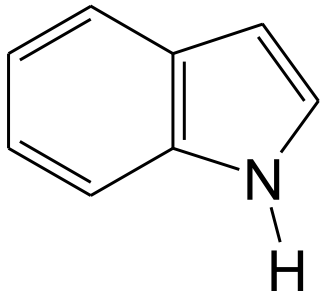
Strecker Synthesis

Treating an aldehyde with ammonia and hydrogen cyanide produces an α-aminonitrile. Hydrolysis of nitrile group of the α-aminonitrile converts the latter to an α-amino acid.



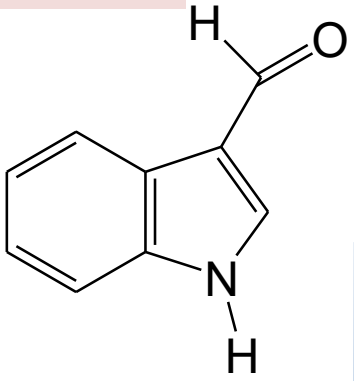
R=H; Glycine R=CH_3-; Alanine

Gabriel Synthesis for Tryptophan:

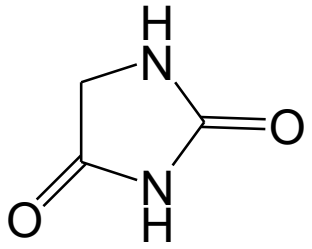


1. $CHCl_3$ & NaOH

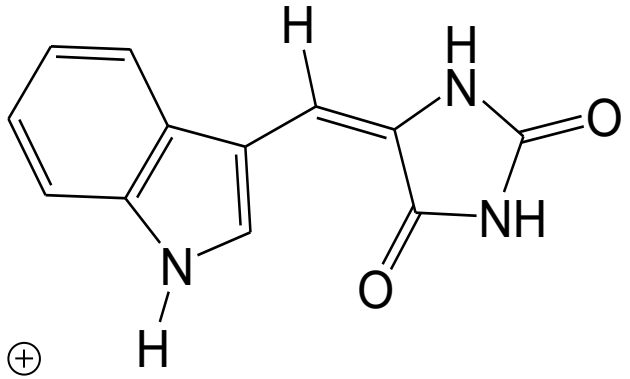
2. H_3O^+



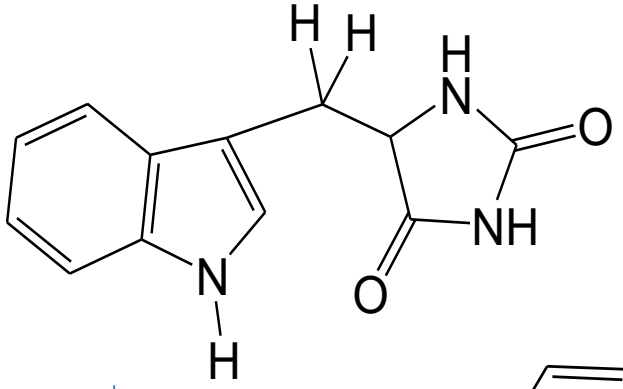
Ac_2O



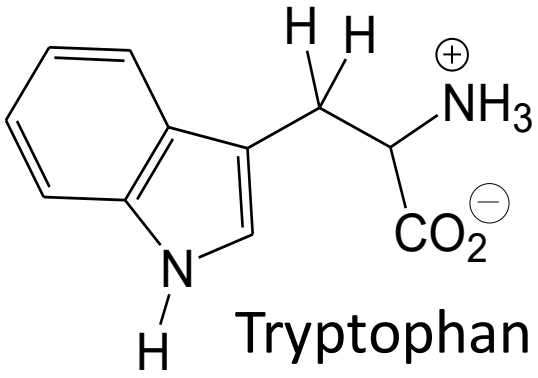
Hydantoin



Na-Hg



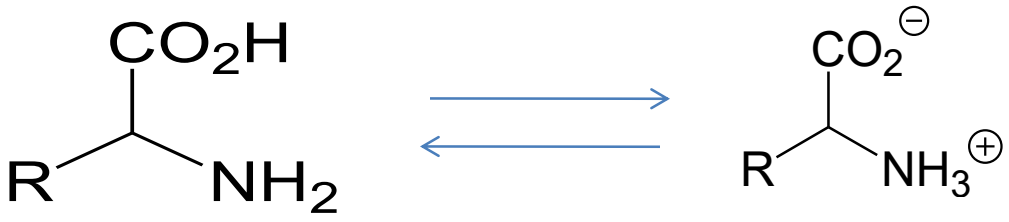
Dil HCl



Tryptophan

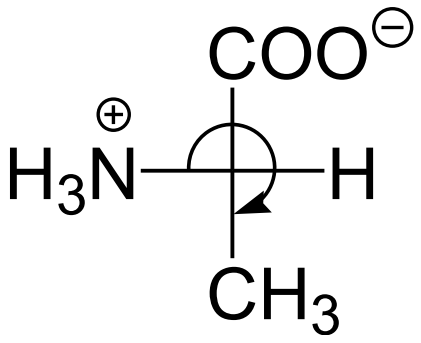
Properties of Amino acids

- Amino acids have high melting point.
- Amino acids have larger dipole-moment than simple amines or simple acids.
- Amino acids are less acidic than most carboxylic acids and less basic than most amines.



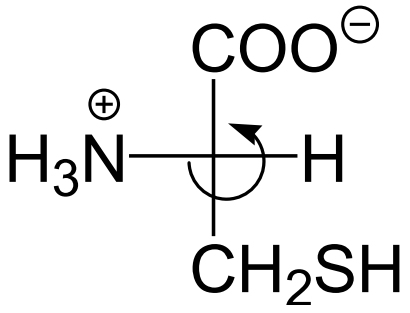
Zwitter or Dipolar ion

Relative and absolute configuration of α-Amino acids



(S)-

L-Alanine

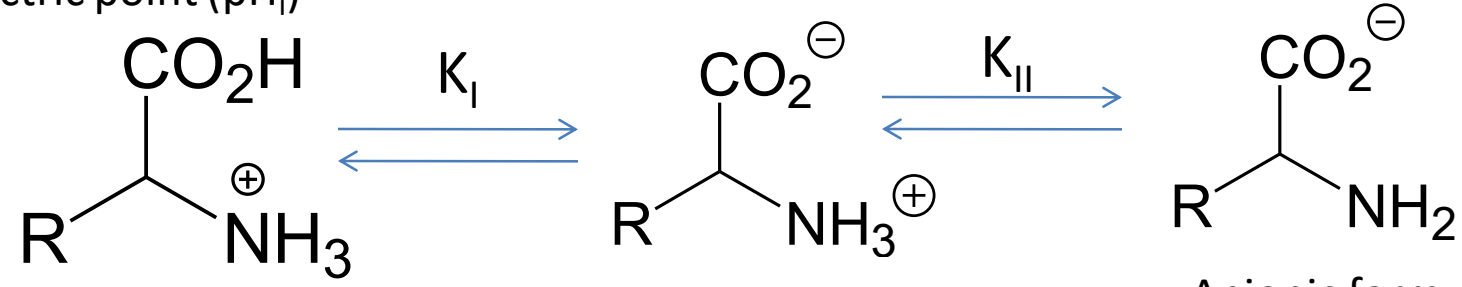


(R)-

L-Cysteine

Iso-electric Point

The pH (for every amino acids) at which there is no net migration of amino acids (to either cathode or anode) under the influence of an applied electric field, is called Iso-electric point (pH_i)

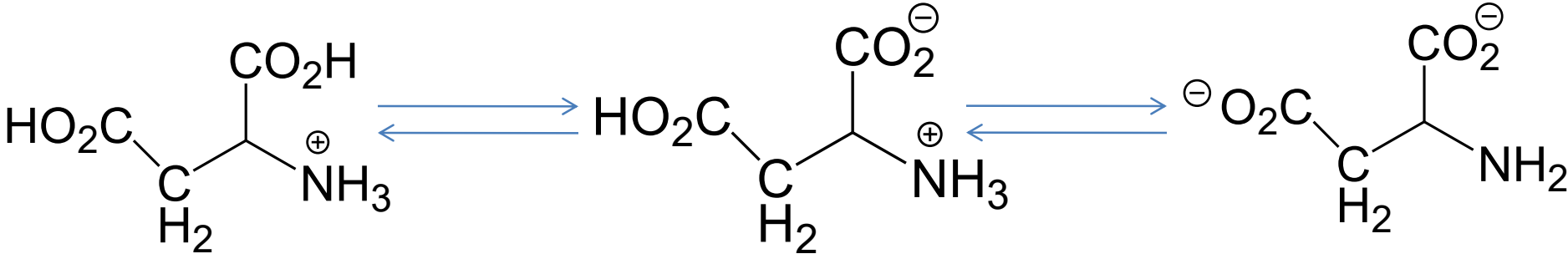


Cationic form
At low pH

Zwitter or Dipolar ion
At iso-electric point

Anionic form
At high pH

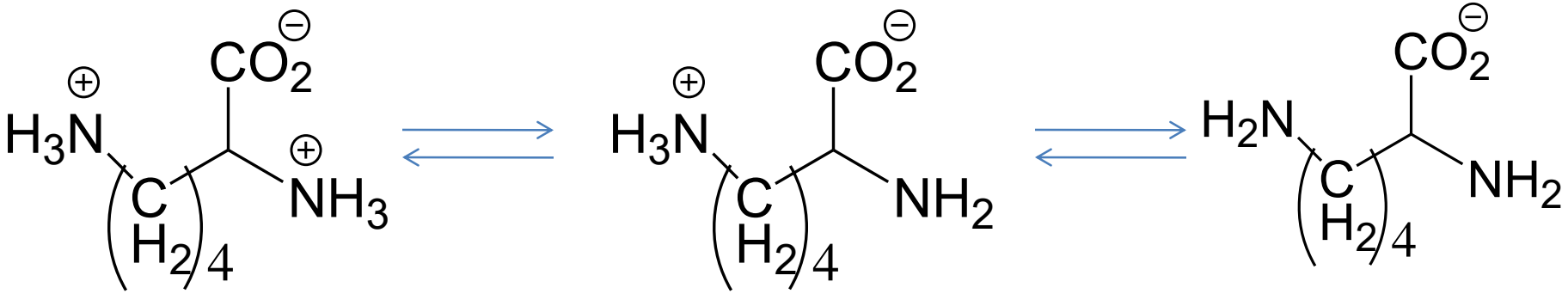
$$pH_i = \frac{pK_I + pK_{II}}{2}$$



Cationic form
At low pH

Zwitter or Dipolar ion
At iso-electric point

Anionic form
At high pH

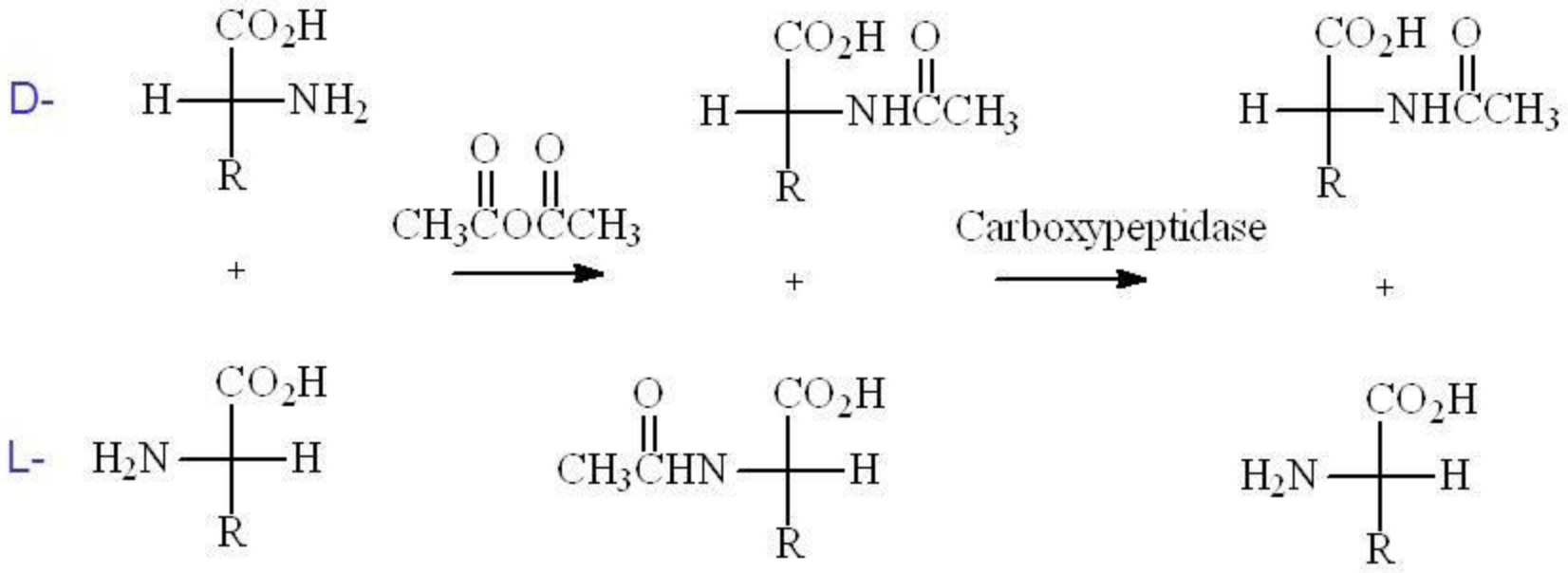


Cationic form
At low pH

Zwitter or Dipolar ion
At iso-electric point

Anionic form
At high pH

Resolution of racemic amino acids



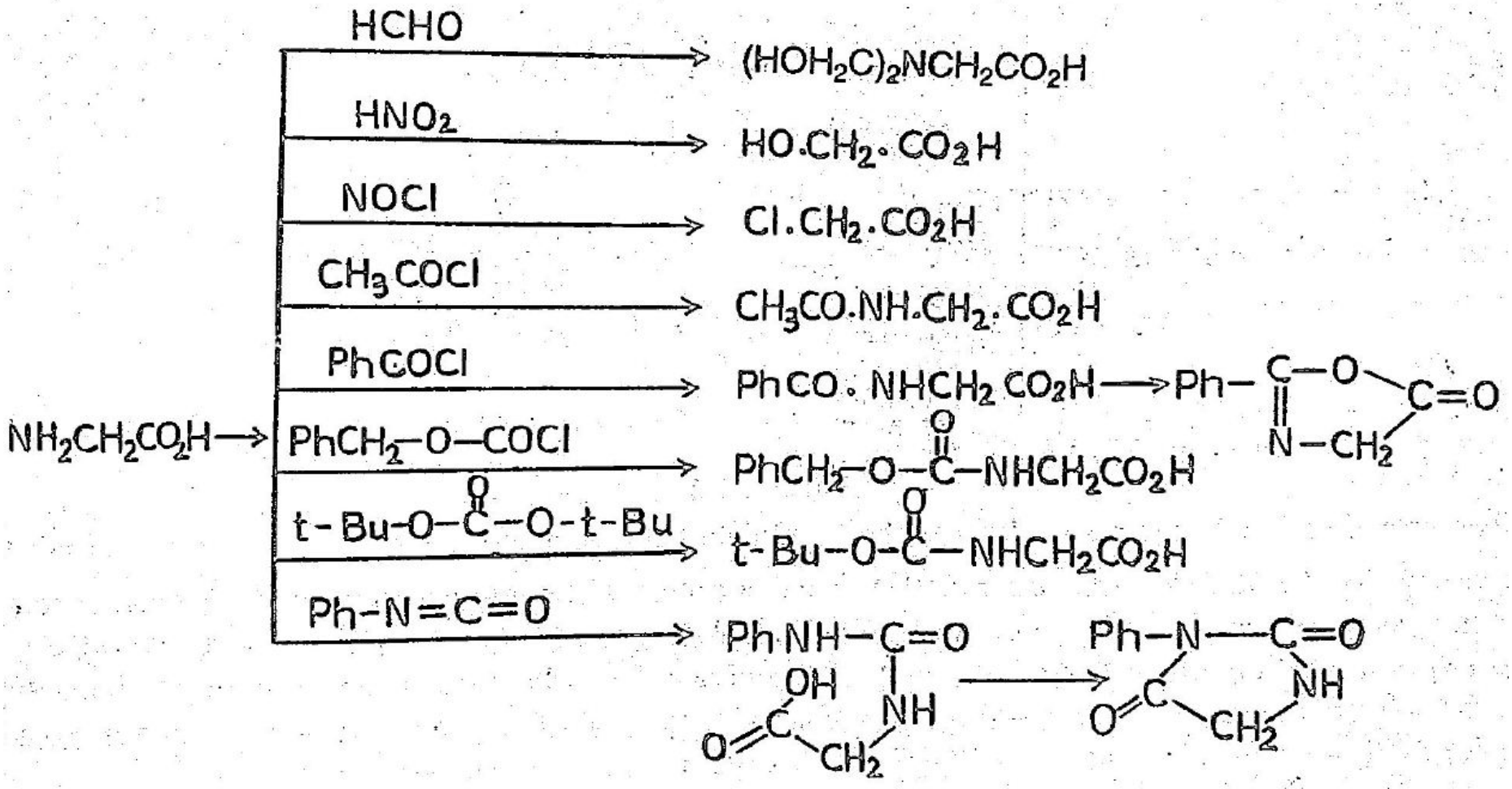
Racemic amino acid

Racemic N-acetyl amino acid

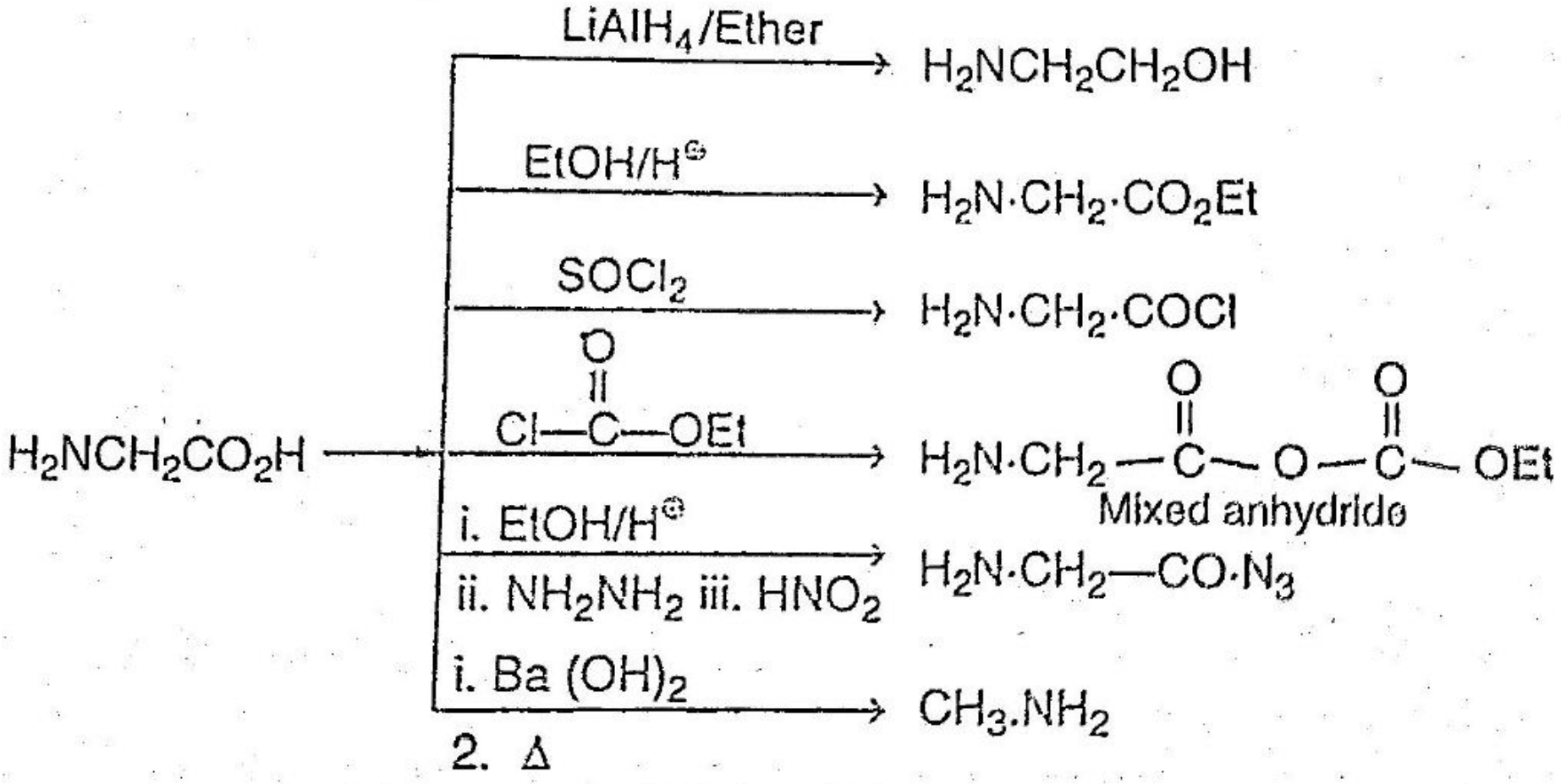
L-amino acid +
D-N-acetylamino acid

Carboxypeptidase hydrolyzes the amide bond ONLY of the L-aa, leaving the unnatural D-N-acetylamino acid unreacted; separation is simple

Reactions of amino acids involving the amino group



Reactions of amino acids involving the carboxylic group



Ninhydrin Test

Negative Ninhydrin Test

Amino acid Absent

Positive Ninhydrin Test

Amino acid Present

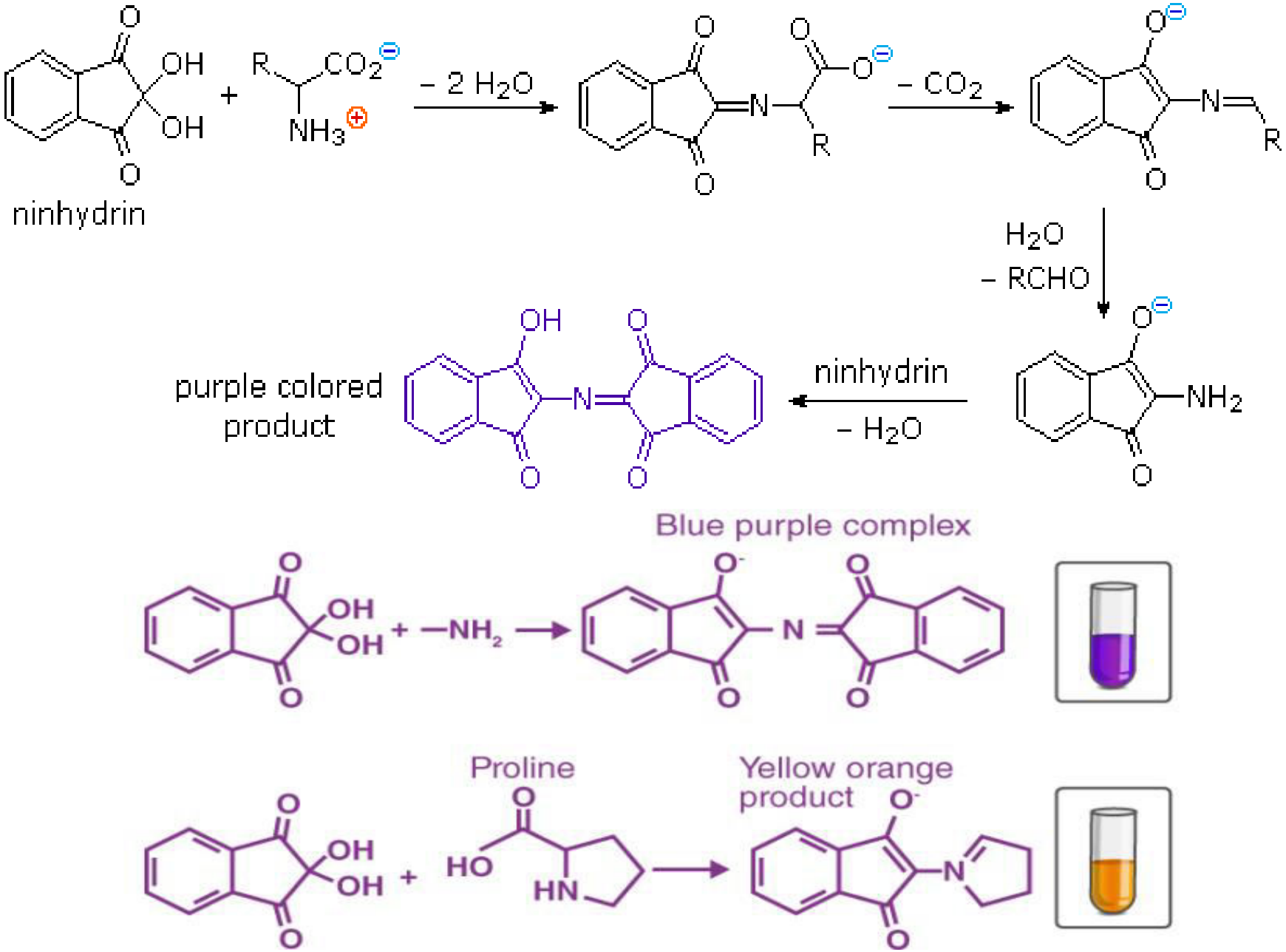
Purple-colored complex present

All amino acids give this colour after reaction withninhydrin except Proline and hydroxyproline Give yellow colour

Proline present

Proline and hydroxyproline Give yellow colour

Mechanism; Ninhydrin Test



Protein

Proteins are complex organic nitrogenous substances formed in all type of living organisms are composed of C,H,O, N and S in varying contents. In some cases phosphorous and other elements such as Cu, Hg, Fe etc may present.

Proteins are bio-polymer of amino acids. When protein are hydrolysed by acids, alkalis or enzymes, a mixture of amino acids is obtained.

Peptides

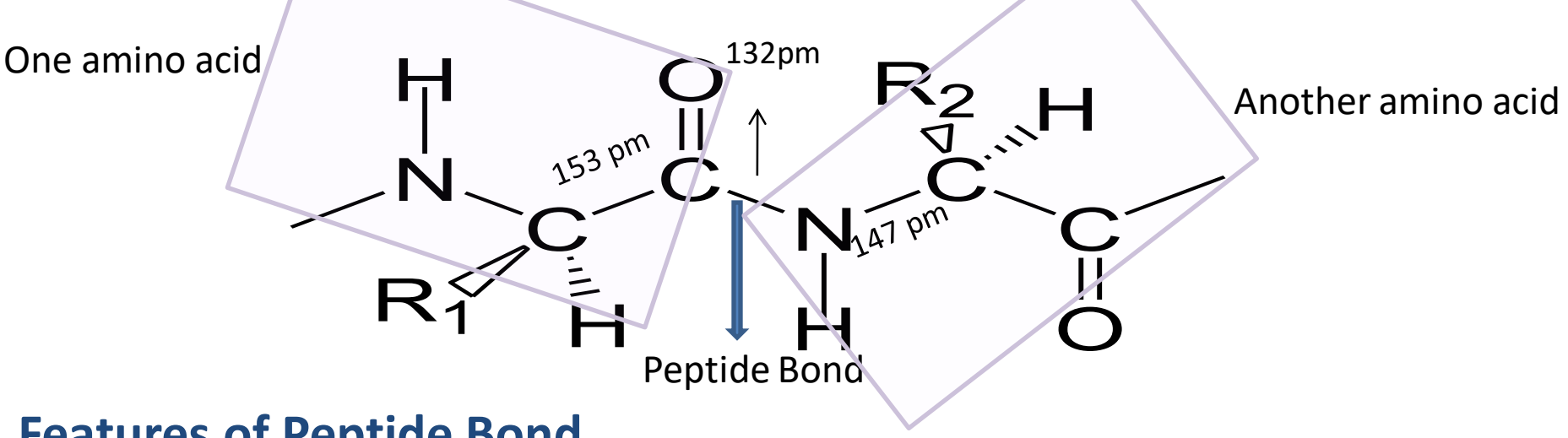
The compound formed by combination of two amino-acids through a peptide bond is called a **dipeptide**. If a third amino-acid joins the dipeptide by forming a peptide bond (new), it is called a **tripeptide**

Oligo-peptides: A peptide containing (3-10) amino acid residues is called an olig- peptide

Polypeptides: A peptide containing more than ten amino acid residues is called an polypeptide

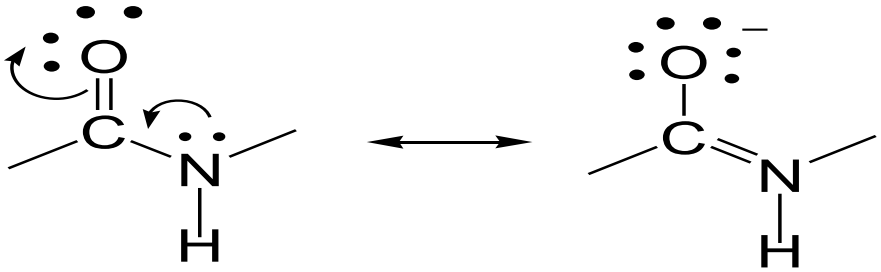
Peptide Bond

Peptide Bond: The amide linkage formed by the reaction of carbonyl group of one amino acid to the amino group of another amino acid is called a peptide bond



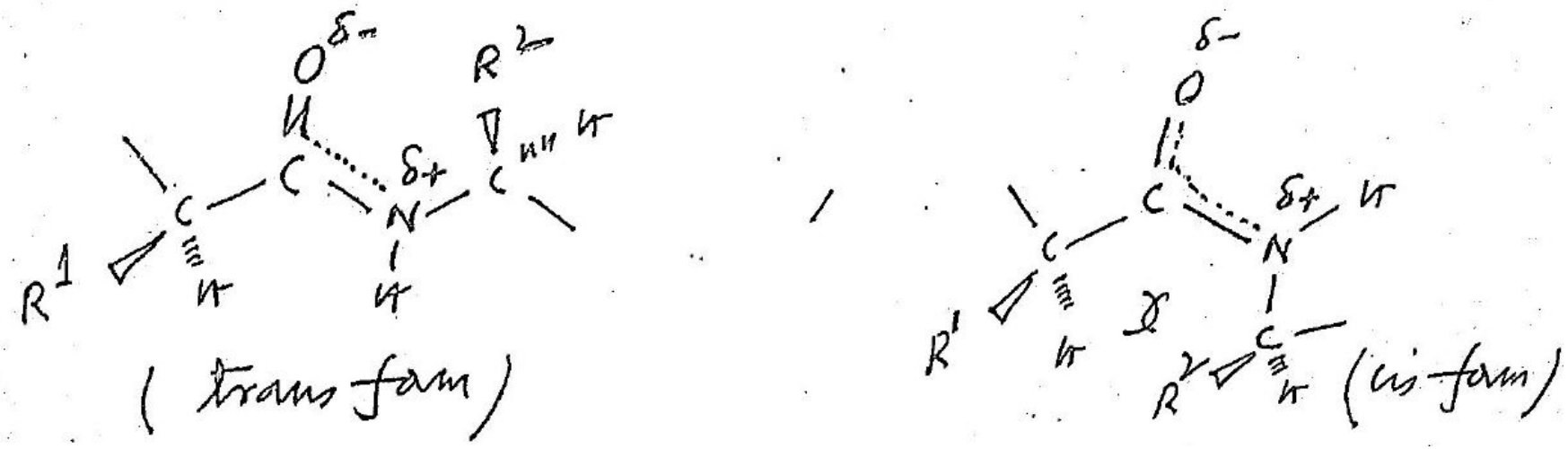
Features of Peptide Bond

1. All the atoms involved in a peptide linkage (-CONH-) are planar. That is 'C' and 'N' atoms are sp^2-hybridised.
2. The carbonyl oxygen atom and the 'H" atom of 'NH' gr are mutually trans.
3. The lone pair electrons on 'N' atom enters in conjugation with adjacent carbonyl (C=O) gr. And thereby the 'C-N' bond gets double bond character.



4. Owing to the double bond character, 'C-N' bond in a peptide is shorter and stronger than normal 'C-N' single bond.
5. Due to the double bond character of 'C-N' bond, free rotation about this bond is restricted And this gives rise to geometrical isomerism.

6.The *trans* form is seen to be about 1000 times more stable than *cis* form.



References:

- **Advanced General Organic Chemistry ; Part 2 by S K Ghos**
- **Organic Chemistry by R T Morrison, R N Boyd & S K Bhattacharjee**
- **Organic Chemistry by F A Carey**
- **Organic Chemistry by Solomons, Fryhle & Snyder**
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