Session-2018-19

Organic Chemistry IV

Presented by:

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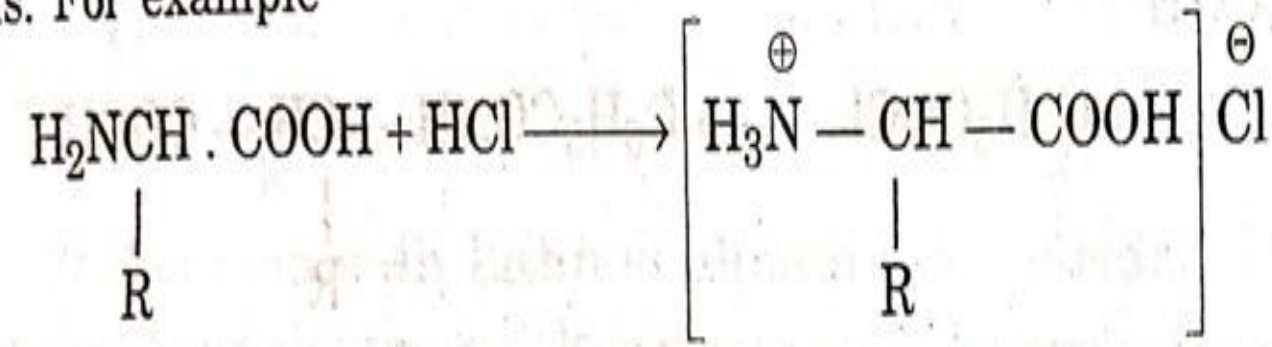
Chemical Properties of Amino Acids

Properties due to -NH_2 Group

(1) Reactions with mineral acids : Amino acids form salts with inorganic acids. For example



Hydrochloride of α-amino acid

Salts of amino acids with mineral acids are sparingly soluble in water. Free amino acids can be obtained from these salts by means of strong organic base like pyridine.

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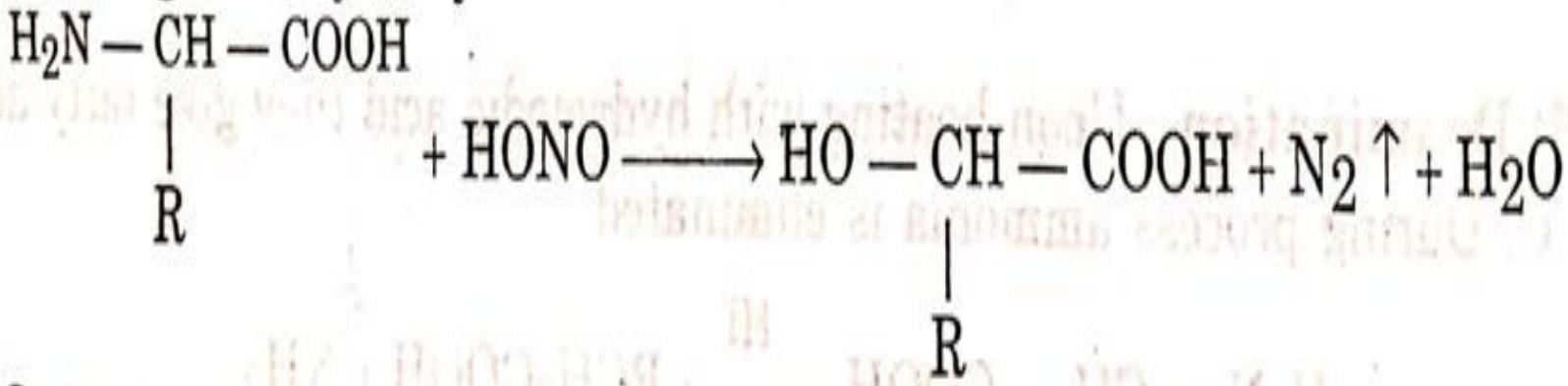
Properties due to -NH_2 Group

(2) Reaction with Nitrous acid : α-Amino acids upon treatment with nitrous acid give α-hydroxy acids

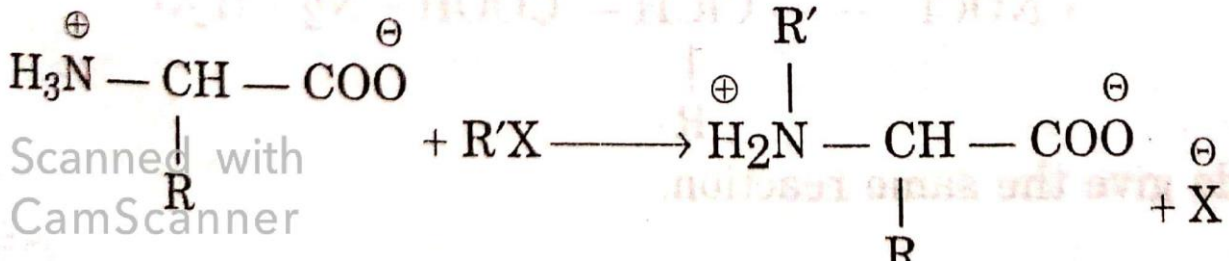


One mole of nitrogen is eliminated in this reaction for each primary amino group (— NH_2). This reaction constitutes the basis for **Van Slyke method** for the determination of free — NH_2 group in proteins.

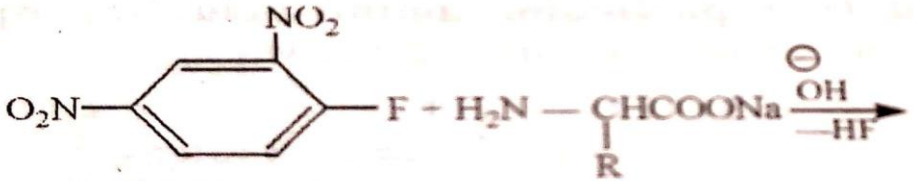
3. Alkylation : Alkylation of

Chemical Properties of Amino Acids

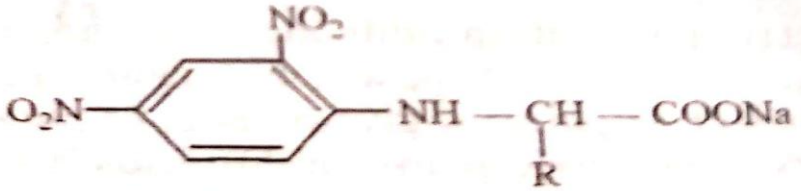
3. Alkylation : Alkylation of amino acids in alkaline medium gives N-alkyl amino acids. Excess of alkyl halide gives quaternary ammonium salts. These salts have Zwitterionic character and are known as **betaines**.



With 2, 4-dinitrofluorobenzene (Sanger's reagent) dinitrophenyl derivatives are formed which are crystalline compounds. This reaction is used in detecting which amino acid of protein or polypeptide has free — NH_2 group.



2, 4-Dinitrofluoro benzene (2, 4-DNF)



2, 4-Dintrophenyl derivative of amino acid

Chemical Properties of Amino Acids

(4) Acetylation and Benzoylation : They can be acetylated with acetyl chloride or acetic anhydride. But benzoylation can be carried out by benzoyl chloride.

$$H_2N-\underset{\displaystyle R}{\underset{|}{CH}}-COOH + CH_3COCl \longrightarrow CH_3CONH-\underset{\displaystyle R}{\underset{|}{CH}}-COOH$$

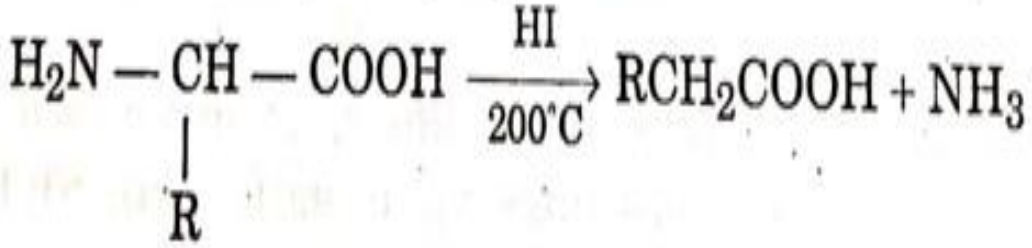
$$H_2N-\underset{\displaystyle R}{\underset{|}{CH}}-COOH + C_6H_5COCl \longrightarrow C_6H_5CONH-\underset{\displaystyle R}{\underset{|}{CH}}-COOH$$

(5) Carbylamine Reaction : As amino acids contain free amino group they give isocyanides with chloroform and alcoholic caustic potash :

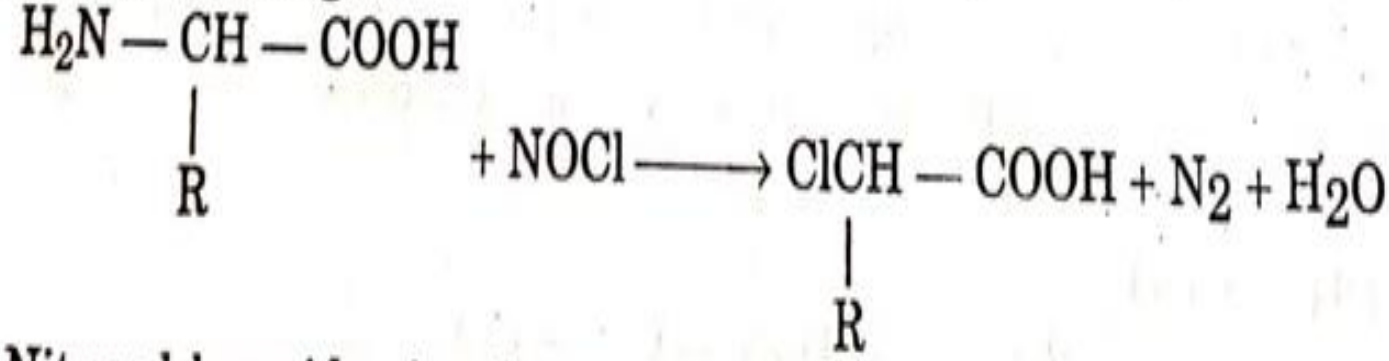
$$H_2N-\underset{\displaystyle R}{\underset{|}{CH}}-COOH + CHCl_3 + 3KOH \longrightarrow CN-\underset{\displaystyle R}{\underset{|}{CH}}-COOH + 3KCl + 3H_2O$$

Chemical Properties of Amino Acids

(6) Deamination : Upon heating with hydroiodic acid they give fatty acids at 200°C. During process ammonia is eliminated.



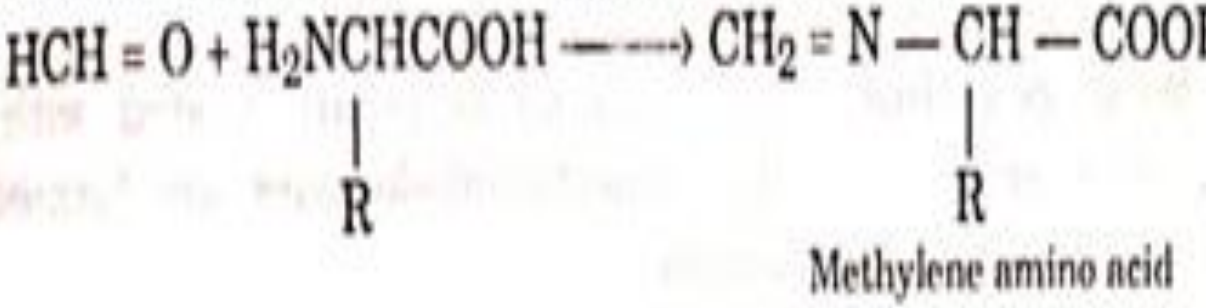
(7) Reaction with nitrosyl chloride : Chloroacids are obtained with the elimination of nitrogen.



Nitrosyl bromide give the same reaction.

Chemical Properties of Amino Acids

(8) Reaction with formaldehyde : With excess of formaldehyde condensation takes place at $-NH_2$ group and methylene amino acid is formed :



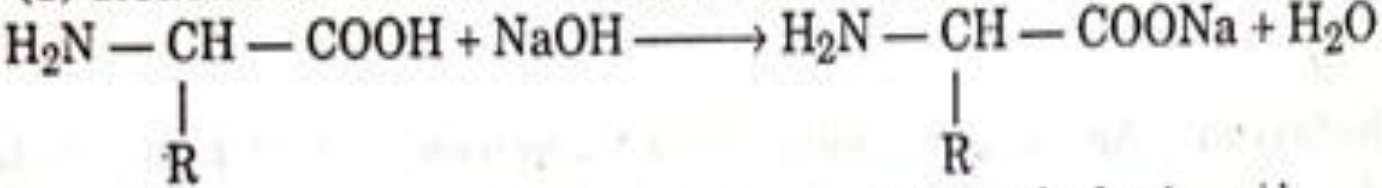
Methylene amino acid

This reaction blocks amino group of amino acid and is used in the **formol titration method (Sorenson method)**. Product of the reaction contains one $-COOH$ group which can be titrated by standard alkali solution using phenolphthalein as an indicator.

Chemical Properties of Amino Acids

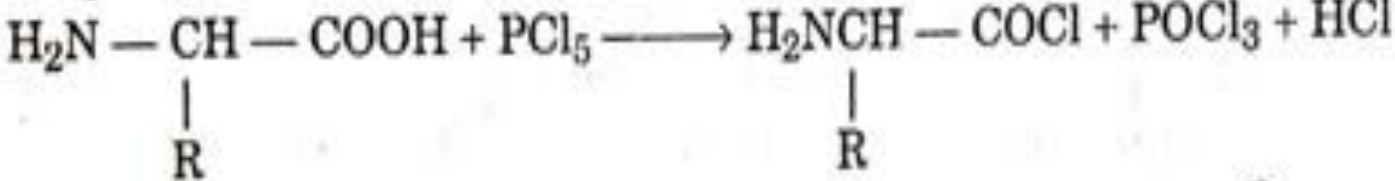
Properties due to -COOH Group

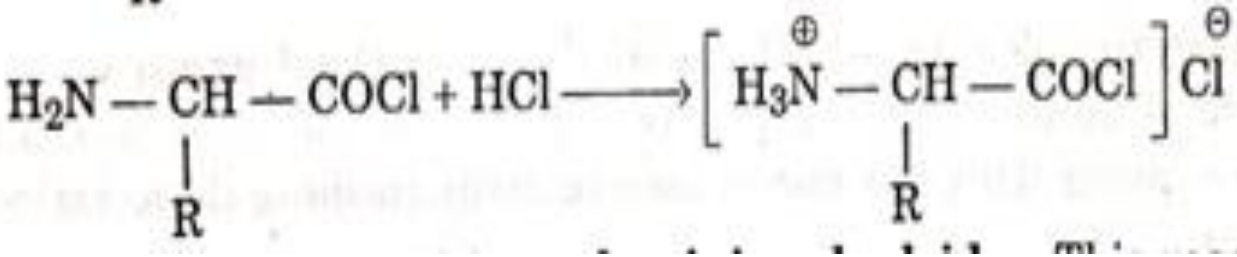
(1) Reactions with alkali : Salt formation takes place :



Sodium salt of amino acid

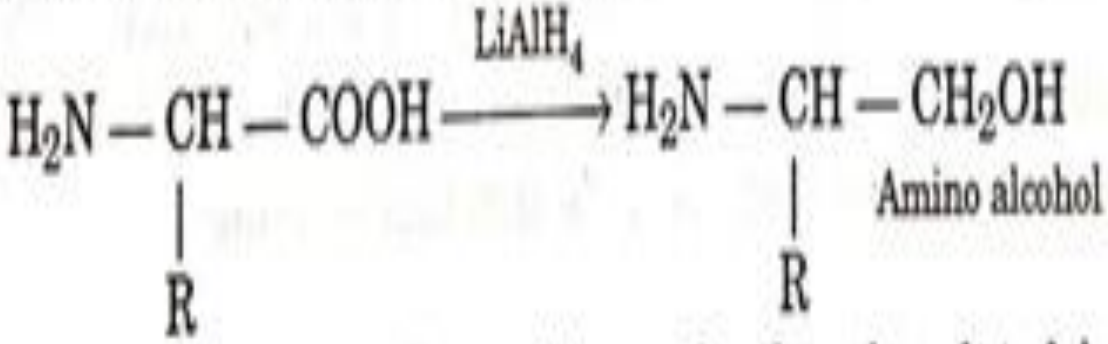
(2) Reaction with acyl chloride : Suspension of amino acid in acid chloride upon treatment with PCl_5 produces the hydrochloride of acid chloride.





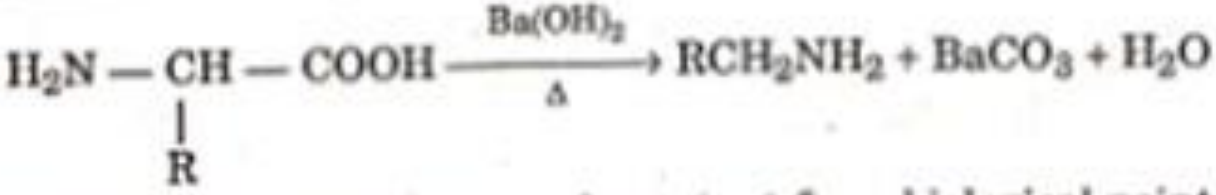
Chemical Properties of Amino Acids

(3) Reaction with Lithium aluminium hydride : This reaction reduces $-COOH$ group to primary alcoholic group and amino alcohols are formed.

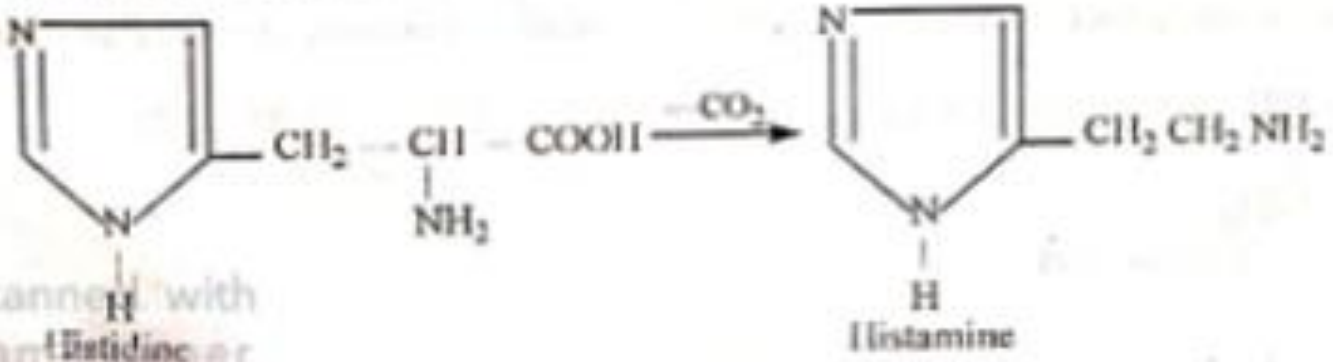


Chemical Properties of Amino Acids

(4) Decarboxylation : Amino acids can be decarboxylated by heating as well as by the action of acids, bases or specific enzymes to primary amines :

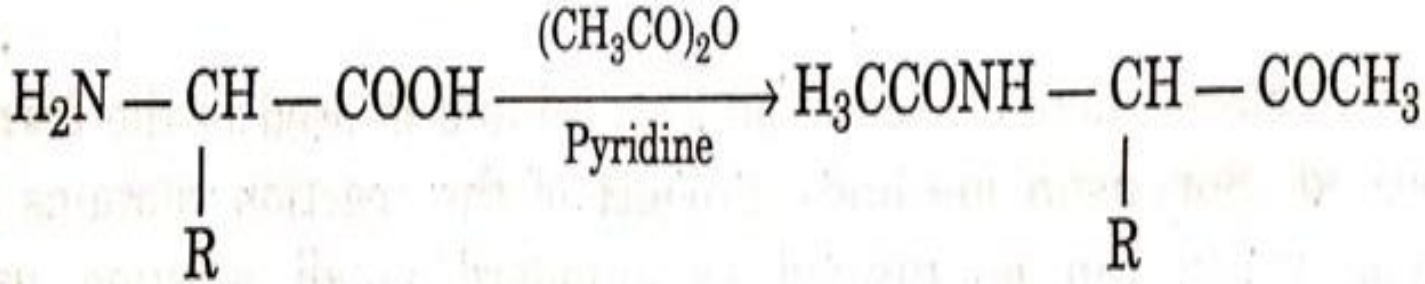


Some decarboxylation reactions are important from biological point of view. For example, decarboxylation of histidine to give histamine.

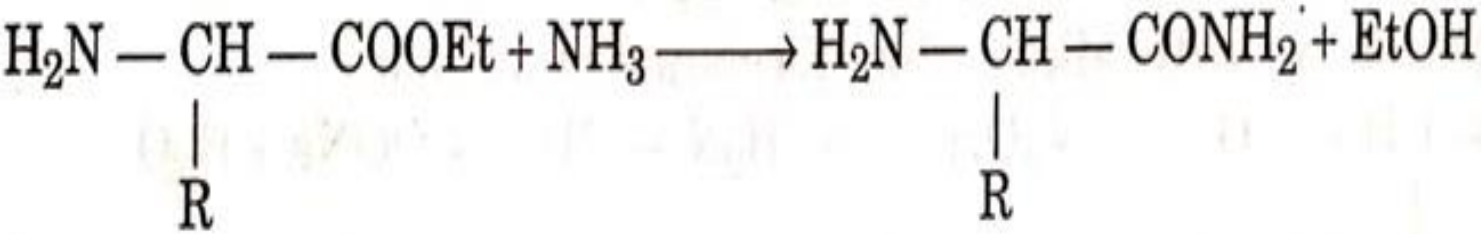


Chemical Properties of Amino Acids

(5) Dakin-West reaction : When amino acids are heated with acetic anhydride in pyridine solution methyl α-acetamido-ketones are formed. This reaction is known as Dakin-West reaction.



(6) Reaction with ammonia : Aminoacid ester form amides upon reaction with ammonia.



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(7) **Chelation** : Amino acids form chelate compounds with heavy metals. For example, when copper oxide is heated with aqueous solution of glycine, chelate compound is formed in the form of deep blue needles.