


CARBOXYLIC ACIDS

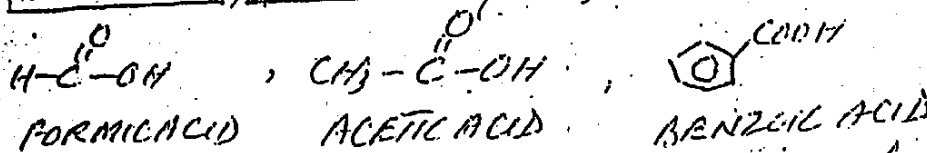
CHAPTER NO. 13 (BOOK II)

INTRODUCTION: Organic compounds having $-COOH$ functional group are called CARBOXYLIC ACIDS. CARBOXYL is combination of carbonyl $-C=O$ and hydroxyl $-OH$ group. Carboxylic acids are divided in two types:

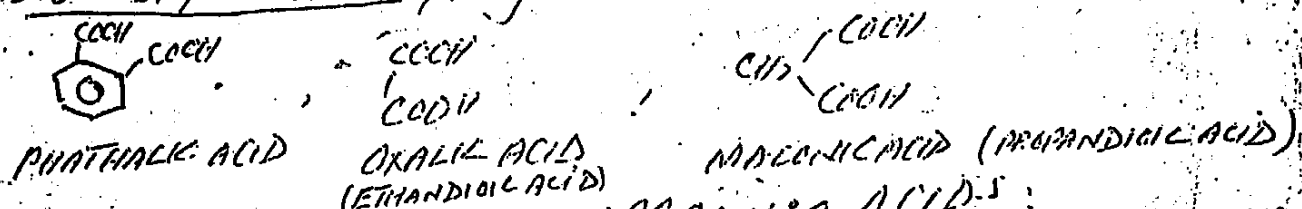
- (i) ALIPHATIC CARBOXYLIC ACIDS: (FATTY ACIDS) (OPEN CHAIN ACIDS)
 $R-C(=O)OH$ e.g. CH_3COOH , CH_3CH_2COOH , $CH_3CH_2CH_2COOH$.
- (ii) AROMATIC CARBOXYLIC ACIDS: $Ar-COOH$. 

CARBOXYLIC ACIDS MAY ALSO BE DIVIDED INTO FOLLOWING TYPES

MONOCARBOXYLIC ACIDS: They have one carboxyl group.

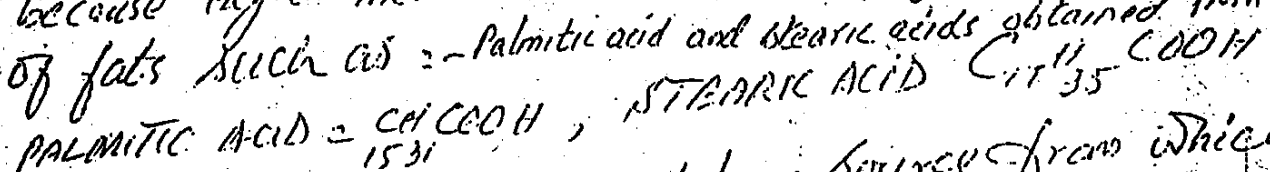


DICARBOXYLIC ACIDS / They have two carboxyl groups.



NOMENCLATURE OF CARBOXYLIC ACIDS

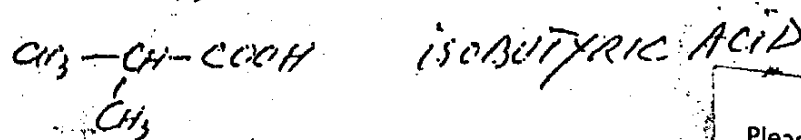
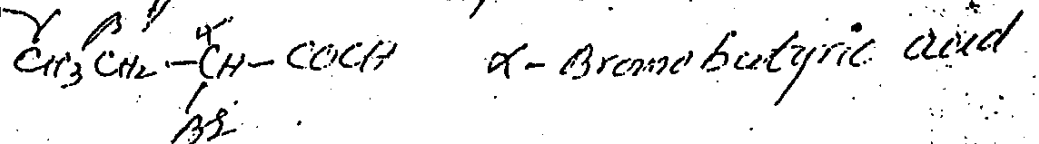
The aliphatic carboxylic acids are called FATTY ACIDS because higher members are obtained from hydrolysis of fats such as:- Palmitic acid and stearic acids obtained from fats.



TRIVIAL NAMES are derived from source from which they are obtained. For example.

- FORMIC ACID } $HCOOH$ OBTAINED FROM RED ANTS.
- ACETIC ACID } CH_3COOH OBTAINED FROM ACETUM (VINEGAR)
- BUTYRIC ACID } $CH_3CH_2CH_2COOH$ " " BUTYRUM (BUTTER)

The position of substituent is mentioned by using Latin alphabets α, β, γ , etc.

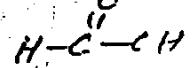


I.U.P.A.C. NOMENCLATURE

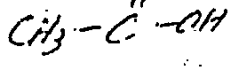
(2)

- THE I.U.P.A.C NAME IS ALKANOIDIC ACID. RULES OF NOMENCLATURE:
- 1) SELECT LONGEST CARBON CHAIN AND WRITE NAME OF PARENT HYDROCARBON
 - 2) REPLACE "E" OF ALKANE NAME BY "OIC ACID"
 - 3) NUMBER CARBON CHAIN FROM CARBOXYLIC GROUP.
 - 4) WRITE NAME OF SUB. IN ALPHABETICAL ORDER WITH POSITION OF EACH SUBSTITUENT.
 - 5) IF TWO CARBOXYL GROUPS ARE PRESENT WRITE SUFFIX

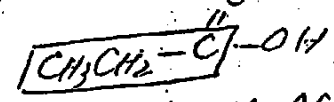
DI-OIC ACIDS :- EXAMPLES ARE GIVEN BELOW.



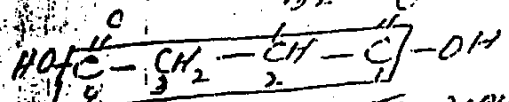
METHANOIC ACID



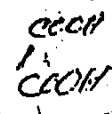
ETHANOIC ACID



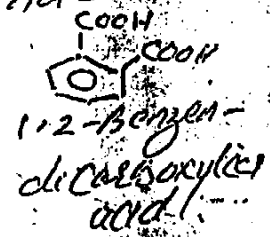
PROPANOIC ACID



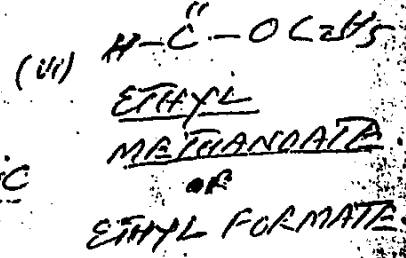
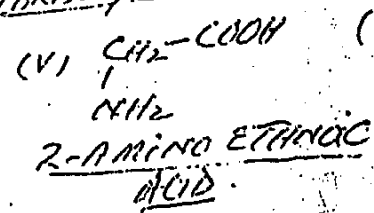
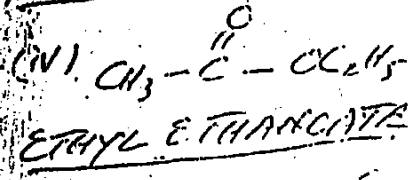
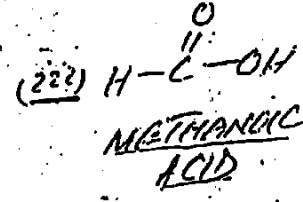
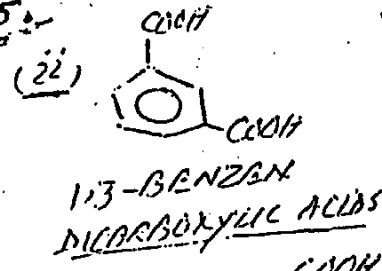
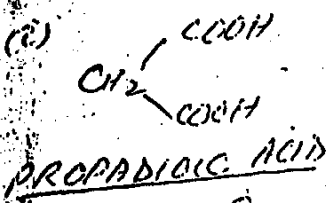
2-BROMO BUTANDIOIC ACID



ETHANEDIOIC ACID

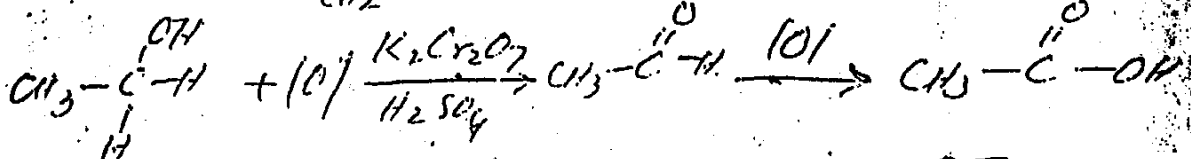
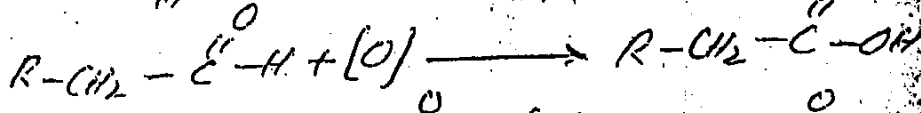
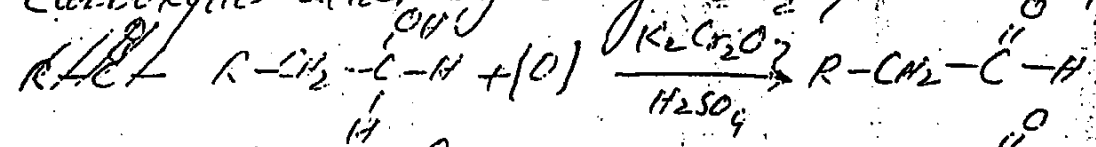


EXERCISE/ Q. NO. 5 :-



"GENERAL METHODS OF PREPARATION"

1. OXIDATION OF β -ALCOHOLS: Alcohols are oxidized to carboxylic acids by using $K_2Cr_2O_7$ and H_2SO_4 .



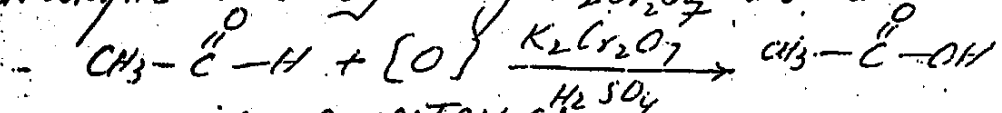
ETHANOL

ETHANAL

ETHANOIC ACID

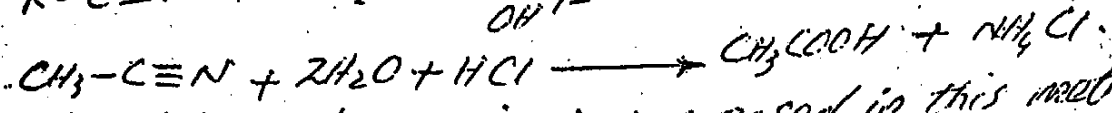
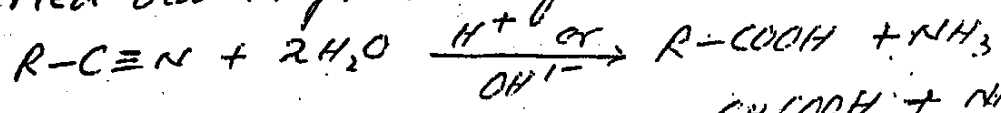
The length of carbon chain is maintained in carboxylic acid.

OXIDATION OF ALDEHYDES Aldehydes are oxidized to carboxylic acids by using $K_2Cr_2O_7$ and conc. H_2SO_4 .

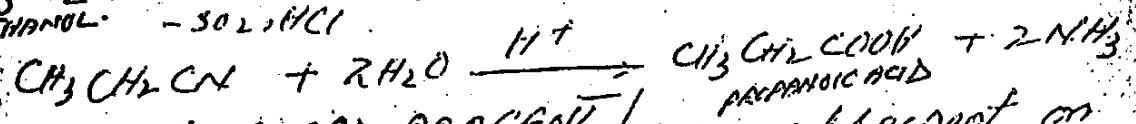
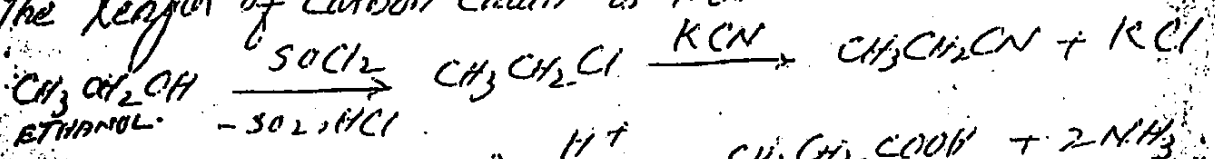


3. HYDROLYSIS OF NITRILES

NITRILES OR CYANIDES on hydrolysis produce carboxylic acids. The reaction is carried out in presence of an acid or base.

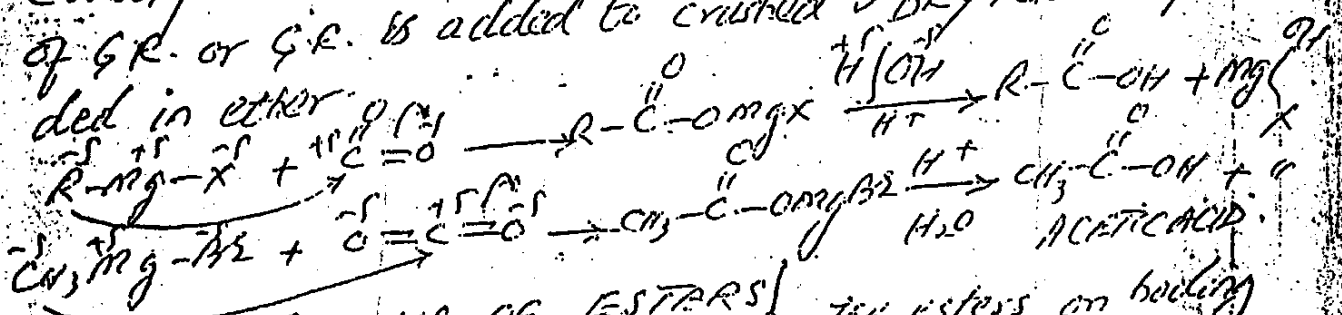


The length of carbon chain is increased in this method



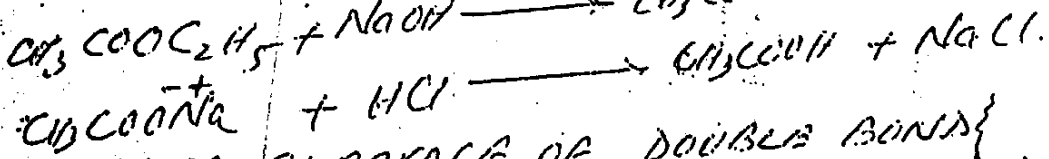
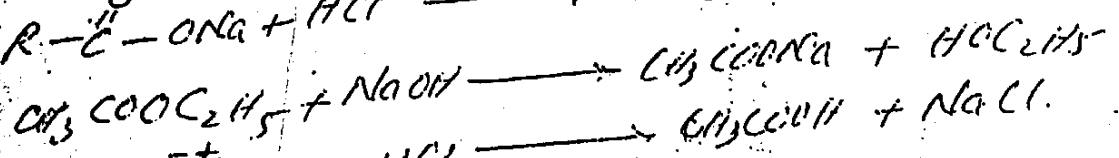
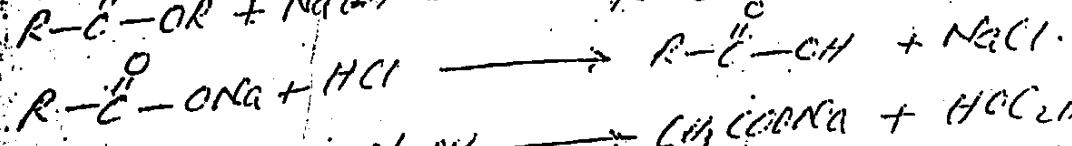
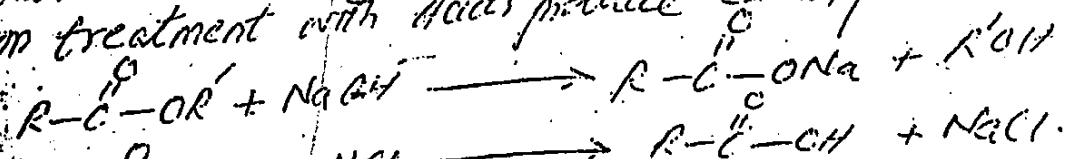
4) FROM GRIGNARD REAGENT

Grignard reagent on reaction with CO_2 followed by hydrolysis produces carboxylic acids. CO_2 is passed through ethereal sol. of G.R. or G.F. is added to crushed DRY ICE suspended in ether.



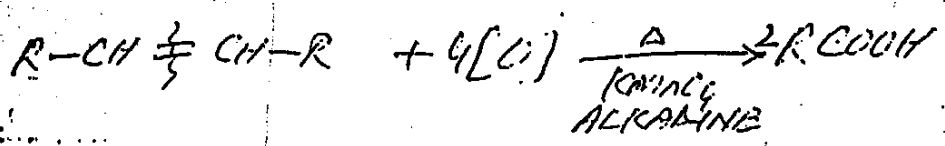
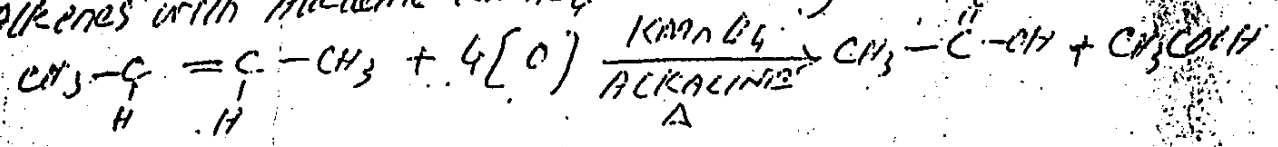
5) BY HYDROLYSIS OF ESTERS

The esters on boiling with conc. Alkalies produce Sodium Salts. These salts on treatment with Acids produce carboxylic acids



6. OXIDATIVE CLEAVAGE OF DOUBLE BONDS

Alkenes with Alkaline $KMnO_4$ are oxidized to acids

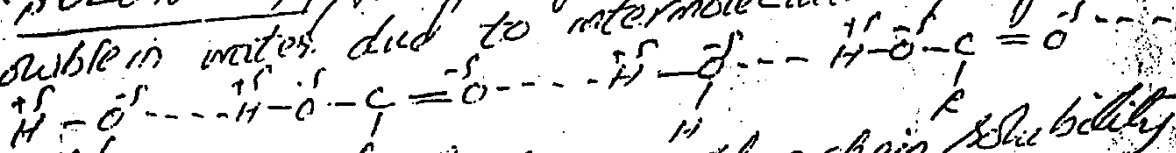


WRITE PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS (4)

COLOUR AND SMELL:-

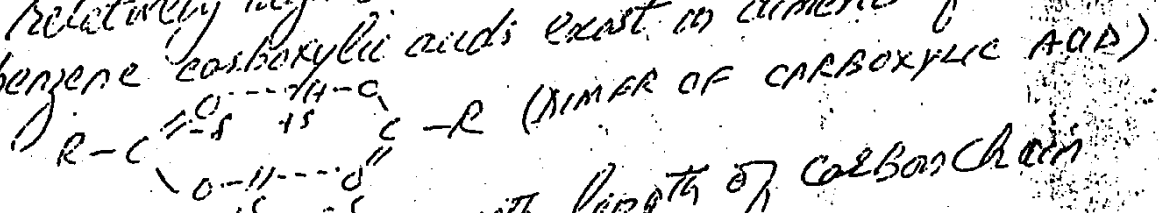
First three carboxylic acids are colourless liquids with pungent smell. The next three are colourless liquids with somewhat unpleasant smell.

2. SOLUBILITY | The first four aliphatic acids are very soluble in water due to intermolecular hydrogen bonding



with increase in length of carbon chain solubility in water decreases.

3. BOILING POINTS | The boiling points of carboxylic acids are relatively high due to intermolecular hydrogen bonding. In benzene carboxylic acids exist in dimeric form.



Boiling points increase with length of carbon chain

HCOOH	CH_3COOH	$\text{CH}_3\text{CH}_2\text{COOH}$
100°C	118°C	151°C (130°)

4. MELTING POINTS | The melting points of carboxylic acids increase irregularly with increase in length of carbon chain. The m.p. of carboxylic acids increase with even number of carbon atoms are greater than next lower and higher members. with odd number of carbon atoms consider following straight chain acids.

$\text{C}_2\text{H}_5\text{COOH}$	$\text{C}_3\text{H}_7\text{COOH}$	$\text{C}_4\text{H}_9\text{COOH}$
m.p. = 251 K	267 K	237 K

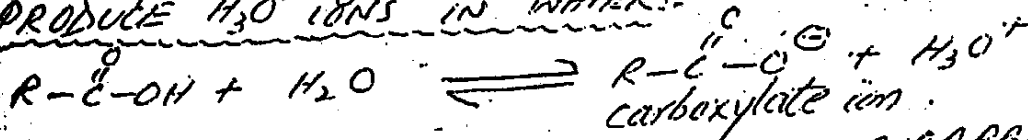
REACTIVITY OF CARBOXYLIC ACIDS | The carboxylic acids show reactions of both carbonyl ($-\text{C}=\text{O}$) and hydroxyl groups. Carboxylic acids undergo following types of reactions

- (i) ACIDIC REACTIONS :- Hydrogen atom of hydroxyl group is involved
- (ii) Reactions in which $-\text{OH}$ is replaced by other group
- (iii) Reactions of carbonyl group as a whole.

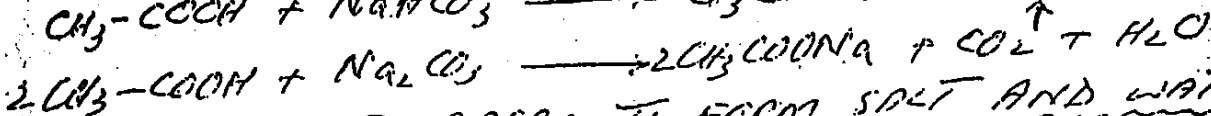
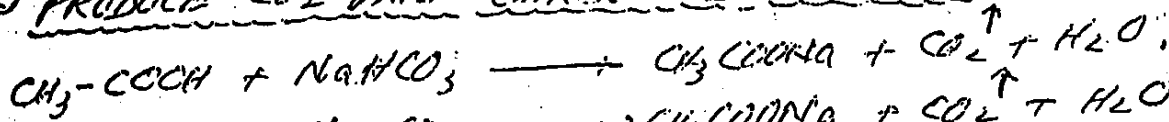
ACIDIC REACTIONS OF CARBOXYLIC ACIDS.

Carboxylic acids are weaker acids than mineral acids (HCl, HNO₃, H₂SO₄, etc.)
 An acid possess following characteristics of acids

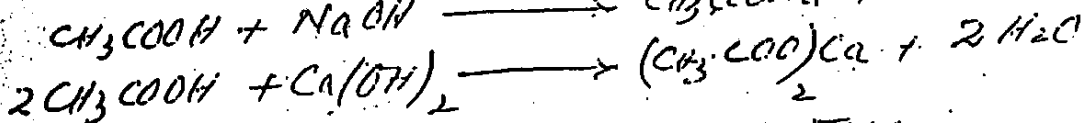
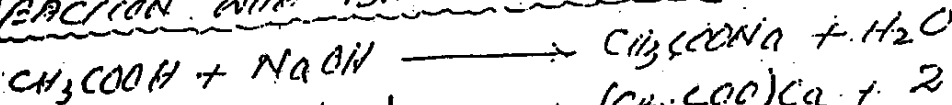
① PRODUCE H₃O⁺ IONS IN WATER.



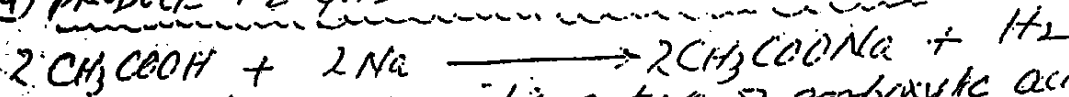
② PRODUCE CO₂ WITH CARBONATE AND BICARBONATES.



③ REACTION WITH BASES TO FORM SALT AND WATER.



④ PRODUCE H₂ GAS WITH ACTIVE METALS.



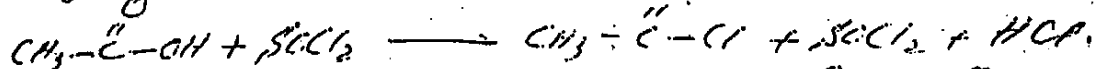
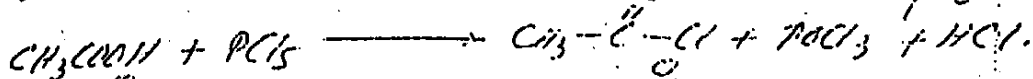
These reactions prove acidic nature of carboxylic acids.

REACTIONS IN WHICH -OH IS REPLACED.

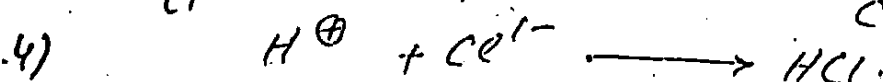
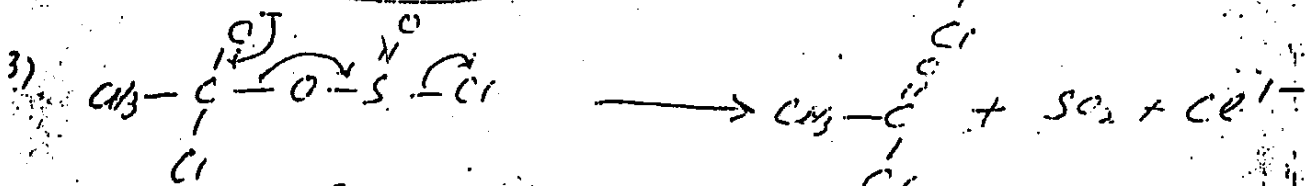
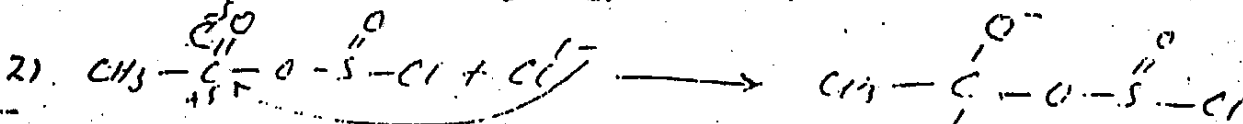
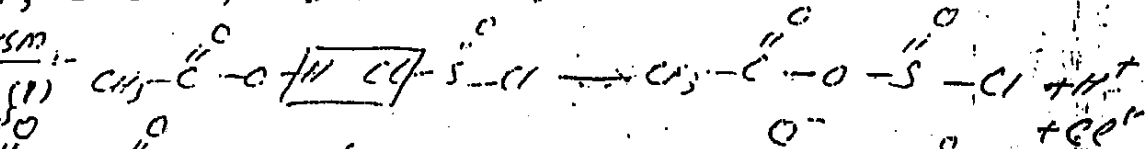
Carbonyl group of carboxylic acids can be easily attacked by nucleophile, the addition is followed by removal of hydroxyl group. The examples of such reactions are ESTERIFICATION, AMIDE AND ACID HALIDE FORMATION.

Q WRITE NOTE ON CONVERSION OF CARBOXYLIC ACIDS INTO ACID HALIDES. ALSO WRITE ITS MECHANISM.

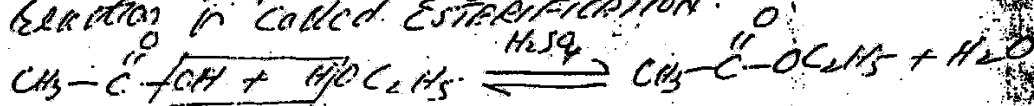
Carboxylic acids can be converted into acid halides by following methods



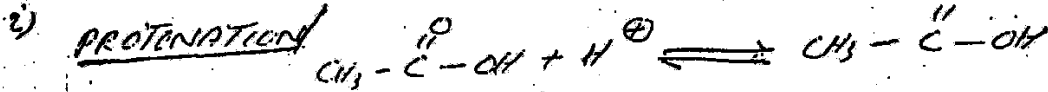
MECHANISM



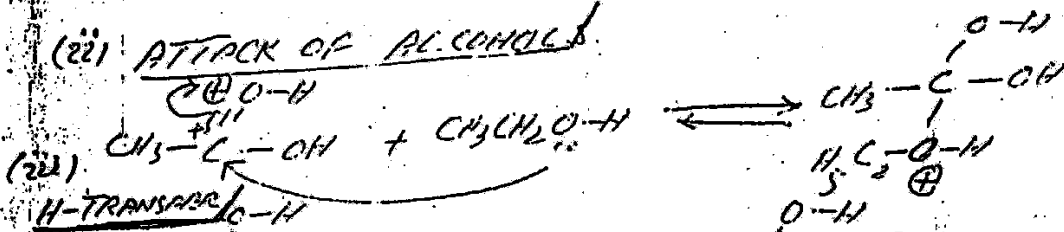
ESTERIFICATION the reaction of carboxylic acids (6) with alcohols in presence of conc. H_2SO_4 produces esters. The reaction is called Esterification.



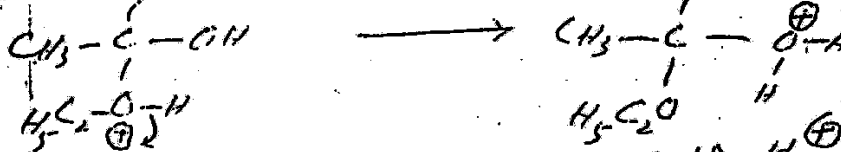
MECHANISM:- It involves following steps



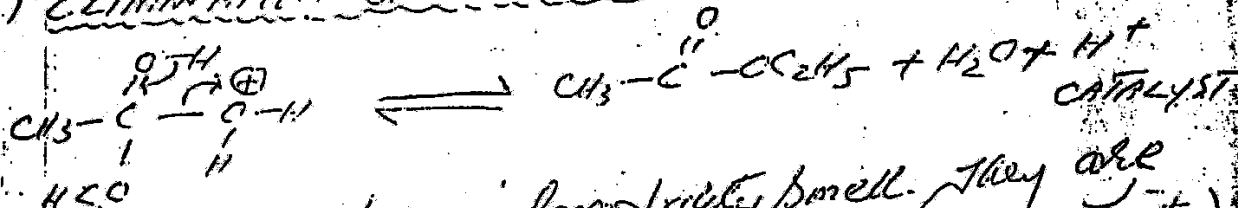
(ii) ATTACK OF ALCOHOL



H-TRANSFER



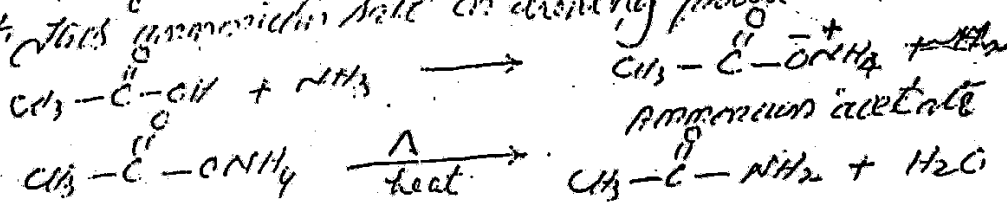
(iv) ELIMINATION OF WATER AND H^+



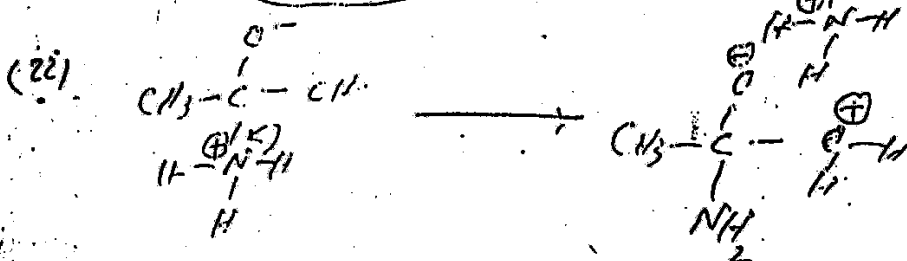
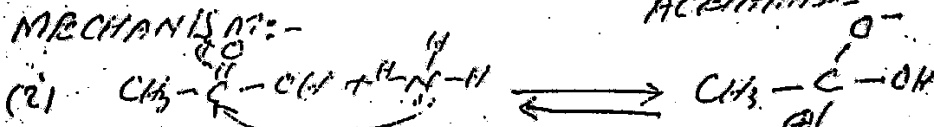
USE OF ESTERS - Esters have pretty smell. They are used as artificial flavours. (Please see Table from text book)

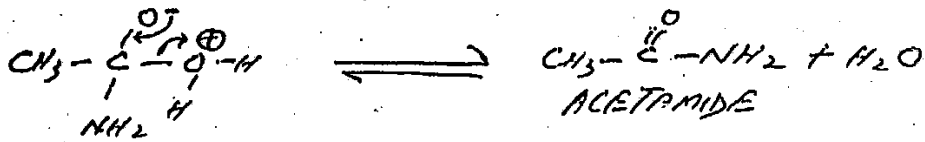
FORMATION OF AMIDE (REACTION WITH NH_3)

Reaction of carboxylic acids with NH_3 produces ammonium salt. This ammonium salt on heating produces amide.



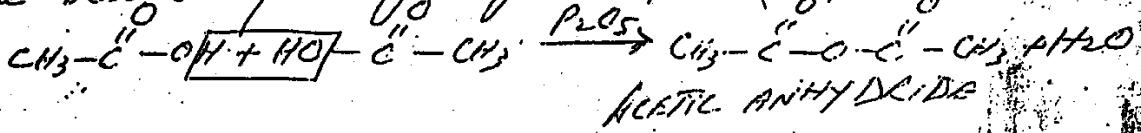
MECHANISM:-





FORMATION OF ACID ANHYDRIDE.

Carboxylic acids are dehydrated to acid anhydride. The best dehydrating agent is P_2O_5 (phosphorus pentoxide).

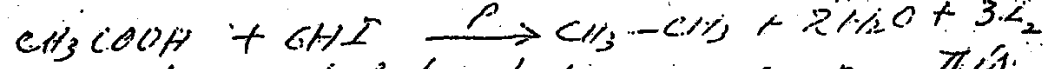


REACTIONS OF CARBOXYL GROUP AS A WHOLE.

Q. WRITE NOTE ON REDUCTION OF CARBOXYLIC ACIDS.

Carboxylic acids are reduced to alcohols on reaction with LiAlH_4 . $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{OH} + (\text{H}) \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O}$

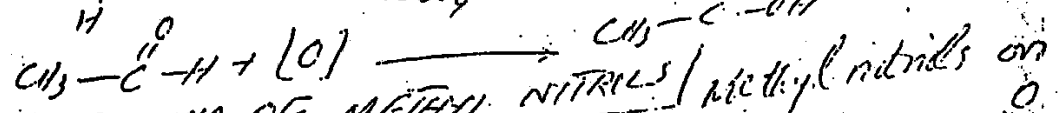
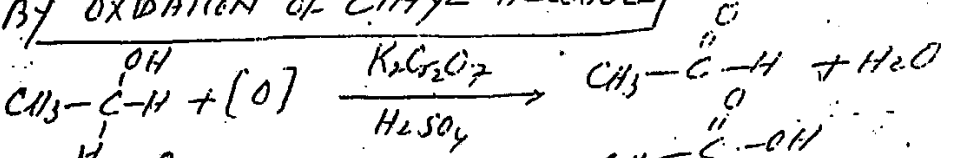
(b) REDUCTION TO ALKANES | Carboxylic acids are reduced to alkanes with HI and red phosphorus.



The carbonyl group is reduced to $-\text{CH}_2$ group in this reaction.

Q. NO. 1 - WRITE LABORATORY AND COMMERCIAL METHODS OF PREPARATION OF ACETIC ACIDS (VINEGAR).

1) BY OXIDATION OF ETHYL ALCOHOL

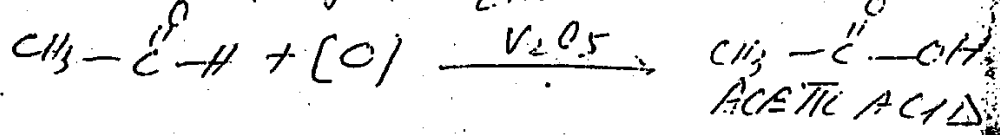
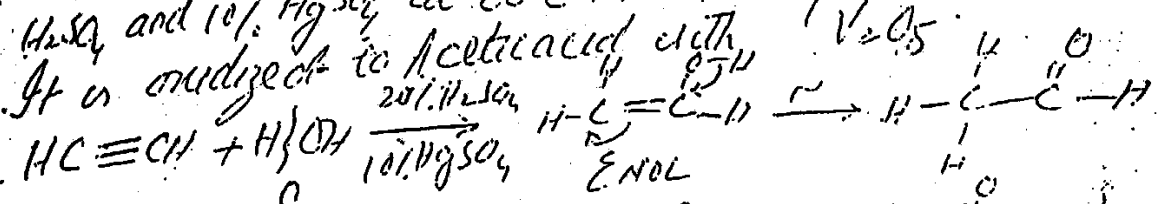


2) HYDROLYSIS OF METHYL NITRILE | Methyl nitrile on hydrolysis produces acetic acid.

$$\text{CH}_3\text{CN} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{NH}_2 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{OH} + \text{NH}_3$$

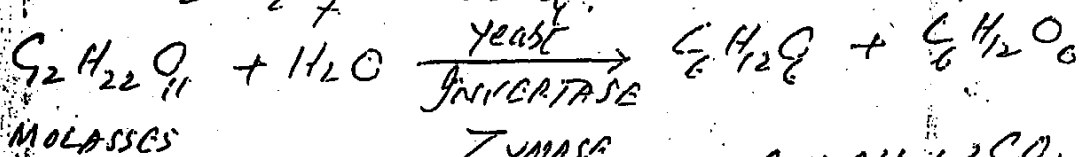
COMMERCIAL METHODS OF PREPARATION.

(a) FROM ACETYLENE | Acetylene is treated with 20% H_2SO_4 and 10% HgSO_4 at 80°C , acetaldehyde is produced.

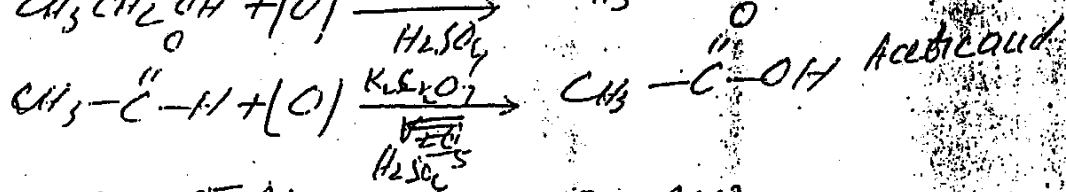
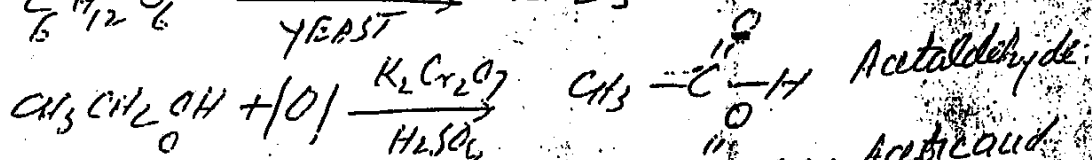
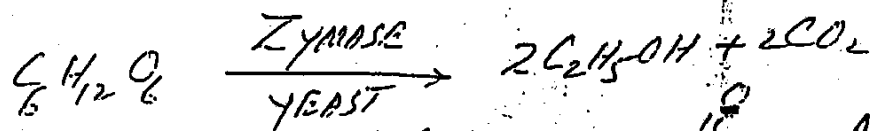


FROM FERMENTATION (OXIDATION OF ETHANOL) (8)

ETHANOL is prepared by fermentation of molasses. It is oxidized to acetaldehyde and then Acetic acid with $K_2Cr_2O_7$ and H_2SO_4 .



MOLASSES



PHYSICAL PROPERTIES OF ACETIC ACID

- 1) It is a colourless liquid with B.P $118^\circ C$.
- 2) Pure acid freezes to ice like solid at $17^\circ C$. Thus it is called glacial acetic acid.
- 3) It has strong vinegar like smell and sour taste.
- 4) It is miscible in water, alcohol and ether in all proportions.

WRITE IMPORTANT USES OF ACETIC ACID

- 1) It is used as a coagulant for latex in Rubber industry.
- 2) Used for manufacture of P.V.C., P.V.A. and Rayon (Cellulose acetate) and silk.
- 3) In medicine it is used as local irritant.
- 4) It is used as a solvent for carrying out reactions.
- 5) It is used in manufacture of pickles.
- 6) In organic chemistry it is used for manufacture of Acetone, acetate and esters.

AMINO ACIDS

The organic compounds having amino group and carbonyl group attached to the same α -carbon are called AMINO ACIDS. Alkyl group "R" is different for different amino acids. Amino acids may also be α , β , γ -amino acids. But all naturally occurring amino acids are α -Amino acids.

Amino acids are basic building block of proteins.

ACIDIC AMINO ACIDS / Amino acids which have an carboxylic acid group in side chain are called Acidic amino acids.

Example Glutamic acid \Rightarrow $\text{COOH}-\text{CH}_2\text{CH}_2-\underset{\text{NH}_2}{\overset{\text{H}}{\text{C}}}-\text{COOH}$
ASPARTIC ACID \Rightarrow $\text{HOOC}-\text{CH}_2-\underset{\text{NH}_2}{\overset{\text{H}}{\text{C}}}-\text{COOH}$

BASIC AMINO ACID / An amino acid having amino group in side chain are called basic amino acids. For example LYSINE.

NON-POLAR AMINO ACID / Side chain is non polar for example Alanine.

Animal and plants contain at the maximum 20 different types of amino acids.

ESSENTIAL AMINO ACIDS / The 10-amino acids which our body cannot synthesize are called essential amino acids. These amino acids must be present in our daily diet. The deficiency of these amino acids can cause diseases.

NON-ESSENTIAL AMINO ACIDS / These amino acids can be synthesized in our body. There are 10-non essential amino acids.

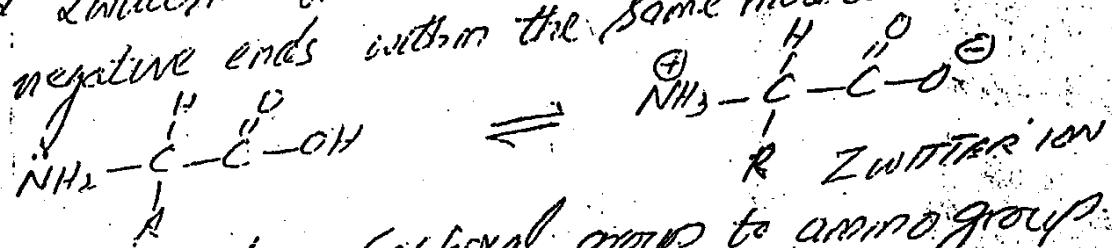
NOMENCLATURE | Amino acids are generally named by their source or some property.

GLYCINE from glyky means sweet. It has sweet taste.

TRYPSINE from tryos means cheese. It was obtained from cheese. Hence named tryos.

ABBREVIATIONS | Each amino acid has been given a three lettered abbreviation. For example "Gly" is an abbreviation of Glycine amino acid. Similarly "Ala" is an abbreviation of Alanine.

Q. WHAT IS ZWITTER ION OR INTERNAL SALT?
 The amino acids exist in the form of a dipolar ion called Zwitterion or internal salt. It has a positive and negative ends within the same molecule.

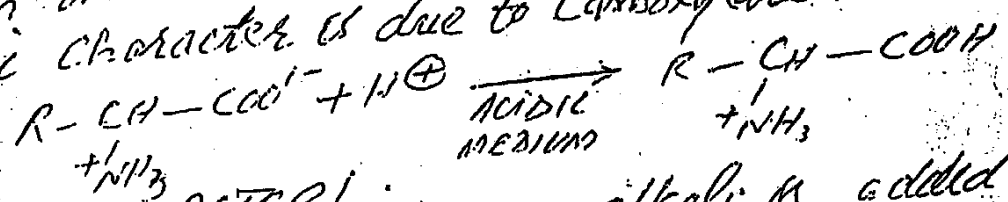


The proton goes from Carboxyl group to amino group. ALL α -AMINO ACIDS exist in the form of Zwitter ion.

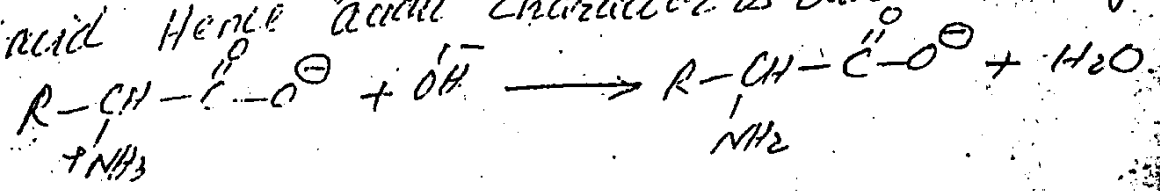
Q. - WRITE ACIDIC AND BASIC CHARACTER OF AMINO ACIDS?

Due to dipolar nature amino acids can act as acids or bases.

BASIC CHARACTER :- The carboxylate ion can accept proton when it is added to acidic medium. Hence basic character is due to carboxylate ion.



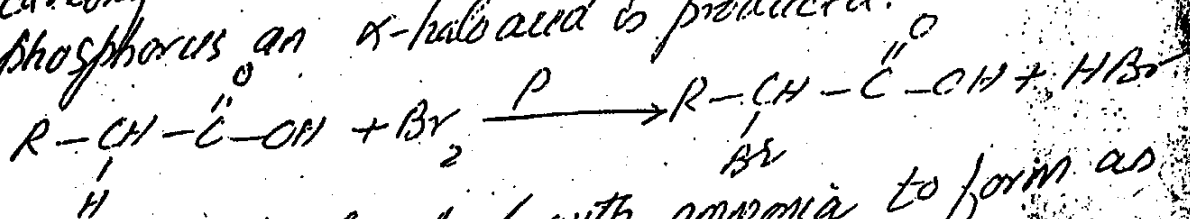
ACIDIC CHARACTER | when an alkali is added to amino acid, -NH_3^{\oplus} group releases proton and act as acid. Hence acidic character is due to -NH_3^{\oplus} group.



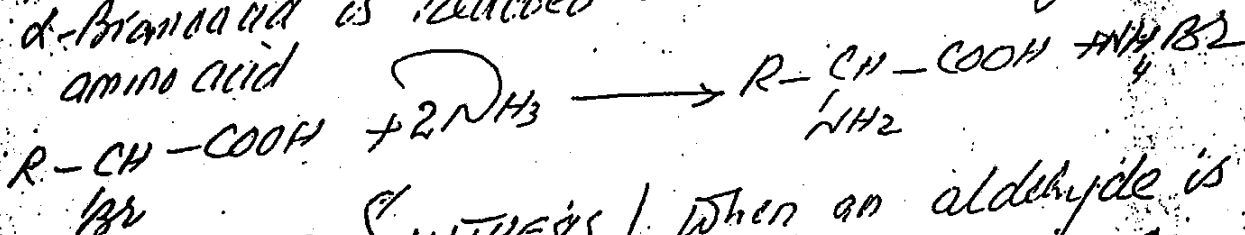
SYNTHESIS OF AMINO ACIDS - Amino acids (10)
 can be synthesized by following reactions.

HELLVOLHARD ZELINSKY REACTION

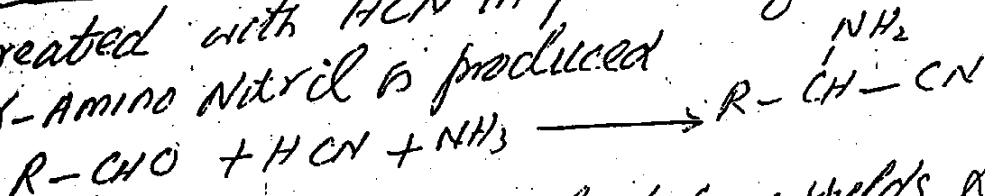
A carboxylic acid is treated with halogen in presence of phosphorus an α -halo acid is produced.



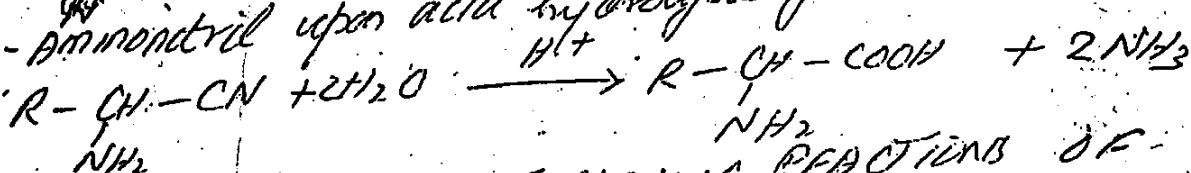
α -halo acid is reacted with ammonia to form an amino acid



STRECKER SYNTHESIS | When an aldehyde is treated with HCN in presence of ammonia, an α -amino nitril is produced

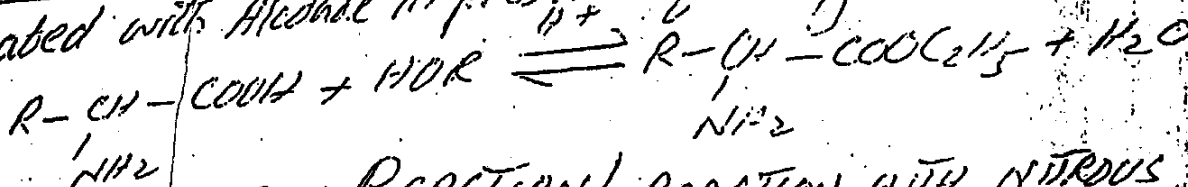


α -amino nitril upon acid hydrolysis yields α -amino acid



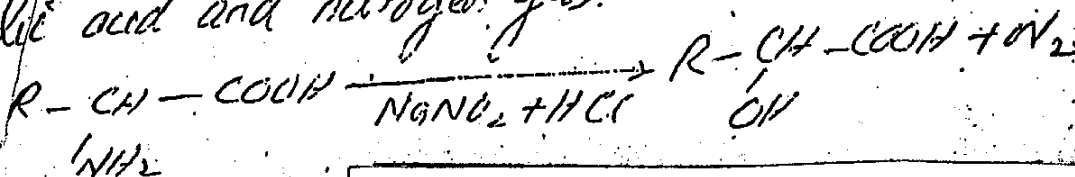
WRITE NOTE ON FOLLOWING REACTIONS OF AMINO ACIDS

1) ESTERIFICATION | Amino acids form amino ester when treated with alcohol in presence of strong acid



2) DEAMINATION REACTION | REACTION WITH NITROUS ACID

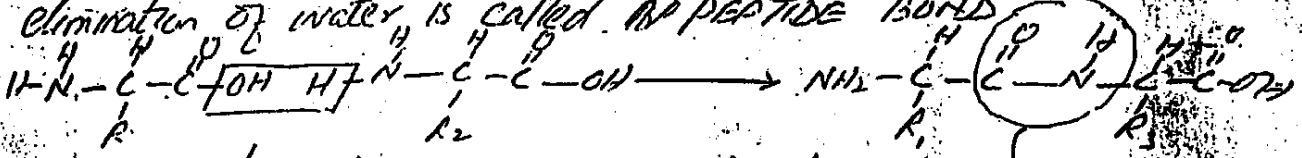
Amino acids react with nitrous acid to produce α -hydroxy carboxylic acid and nitrogen gas.



3. NINHYDRIN TEST / Ninhydrin reacts with amino acids to produce an intensely blue ~~coloured~~ violet product. This reaction is used to visualize amino acids separated by paper chromatography.

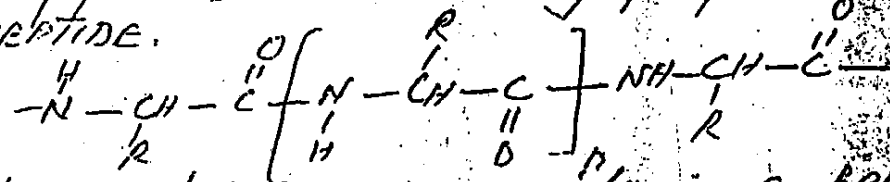
DEFINE THE FOLLOWING TERMS

PEPTIDE BOND: The condensation between two amino acids with elimination of water is called PEPTIDE BOND.



The carboxyl group of one amino acid gets condensed with amino group of other amino acid with elimination of water. (PEPTIDE LINKAGE)

PEPTIDES: The compounds having peptide bonds are called PEPTIDES. If a large number of amino acids are joined by peptide bond the resulting polymer is called POLYPEPTIDE.



Depending upon number of amino acids in a peptide, they may be dipeptide, tripeptide, polypeptide. A PEPTIDE having MW upto 10,000 is called POLYPEPTIDE.

PROTEIN: A polypeptide having molecular mass more than 10000 is called PROTEIN.