B.Sc. IV Semester

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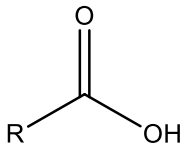
CARBOXYLIC ACIDS

- Organic compounds containing carboxyl group (- COOH) are called carboxylic acids .

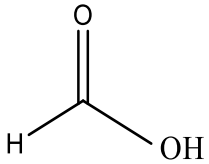


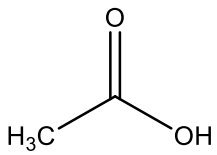
- carboxylic acids are classified as mono , di ,and tri carboxylic acids depending upon the number of carboxyl groups present.
-
- Mono carboxylic acid CH_3COOH Acetic acid

  Di carboxylic acid HOOC- COOH Oxalic acid

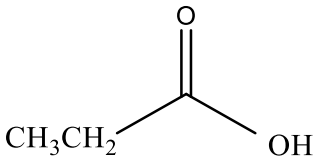
Naming Carboxylic acids

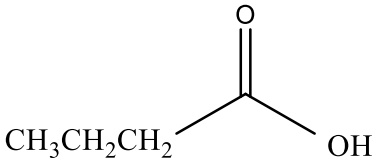
- In systematic nomenclature (IUPAC) , carboxylic acid is named by replacing the terminal " e " of the alkane name with "oic acid ".





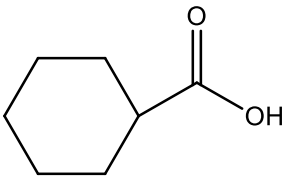
Systematic name:	methanoic acid	ethanoic acid
Common name :	formic acid	acetic acid
parent alkane:	methane	ethane



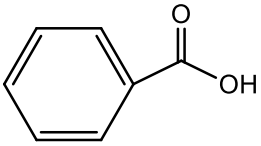


Systematic name:	propanoic acid	butanoic acid
Common name :	propionic acid	butyric acid
parent alkane :	propane	butane

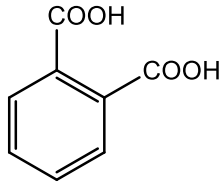
- Carboxylic acids containing six or fewer carbons are frequently called by their common names
- Carboxylic acids in which carboxyl group is attached to a ring are named by adding " carboxylic acid" to the cyclic compound.



cyclohaxanecarboxylic acid



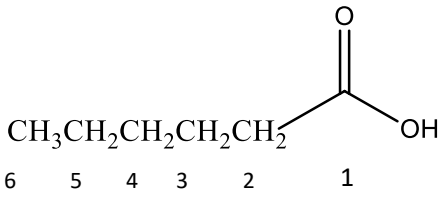
benzenecarboxylic acid
benzoic acid



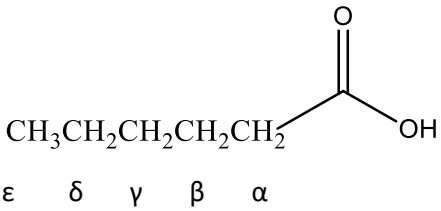
1,2-benzenedicarboxylic acid

Naming Carboxylic acid with substituent

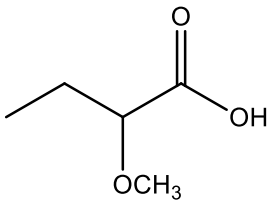
- In systematic nomenclature, the carbonyl carbon is always the C-1 .
- The position of the substituent is designated by a number.
- In common nomenclature the position of the substituent is designated by a lower case Greek letter and the carbonyl is not given a designation .

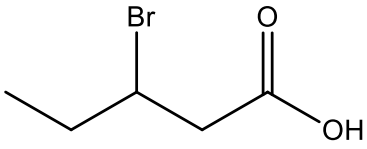


systematic nomenclature



common nomenclature





Systematic name : 2- methoxy butanoic acid

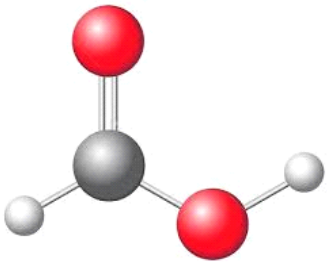
Common name: α-methoxy butyric acid

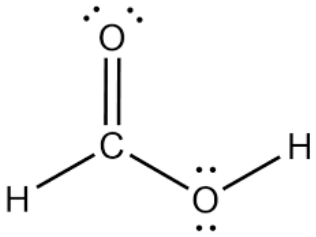
3-bromopentanoic acid

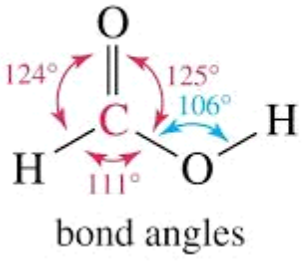
β-bromo valeric acid

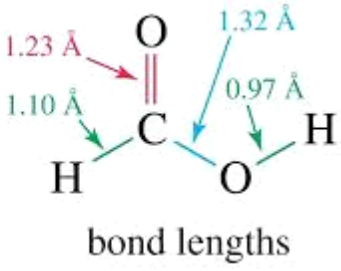
STRUCTURE OF CARBOXYLIC ACIDS

The carbon of carboxyl group is sp^2 hybridised . The carbon utilizes it's three sp^2 orbitals to form three sigma bonds, one bond to carboxyl oxygen, second to oxygen of -OH group and the third to hydrogen or alkyl group. The carboxyl group (-COOH) is planar in structure with hydroxyl hydrogen lies out of the plane. The unhybridised p- orbital of carboxyl carbon forms a pi -bond with p -orbital of carboxyl oxygen.





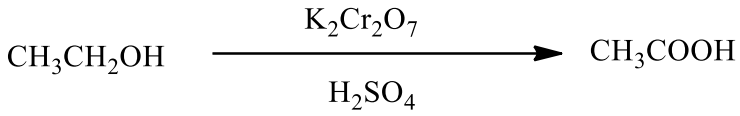




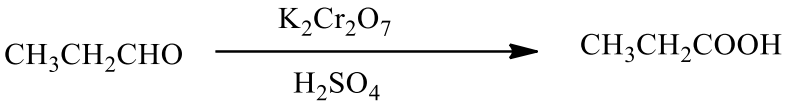
Structure of formic acid

SYNTHESIS OF CARBOXYLIC AICDS

1. By the oxidation of primary alcohols and aldehyde

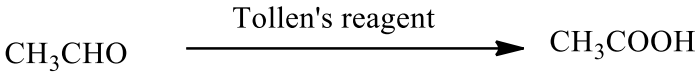


primary alcohol



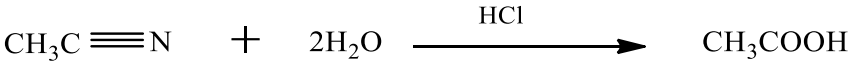
aldehyde

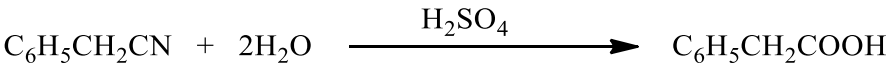
Aldehydes are easily oxidised to corresponding carboxylic acid with mild oxidising agent.



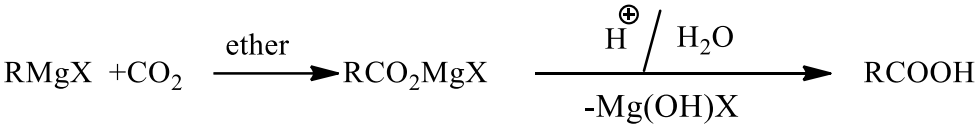
acetaldehyde acetic acid

2. By the hydrolysis of nitriles with acid or alkali

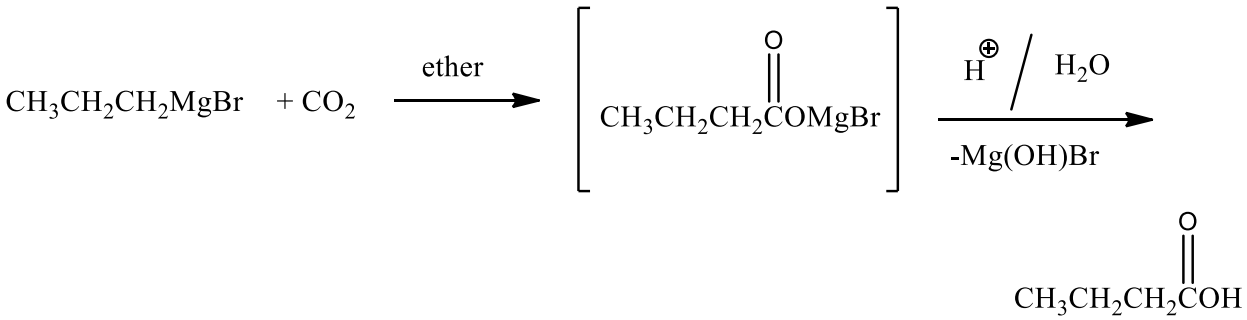




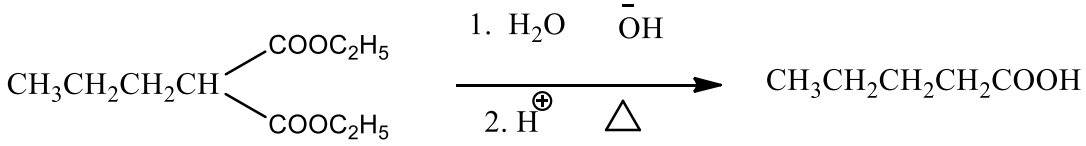
3. By the reaction of Grignard reagent and carbon dioxide

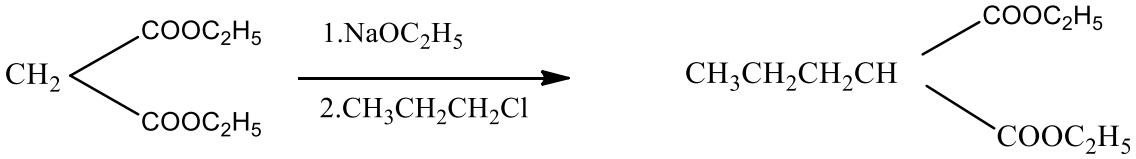


A new carbon -carbon bond is formed in this reaction

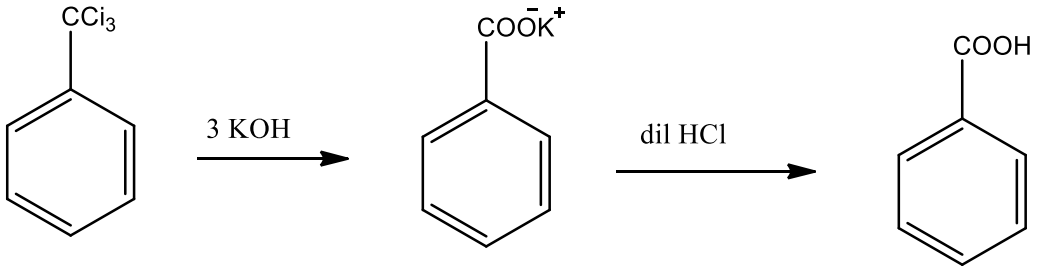


4. By the hydrolysis of malonic ester

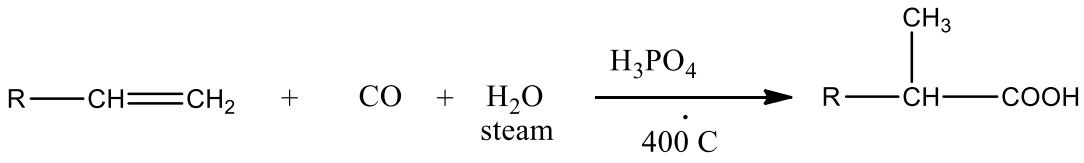




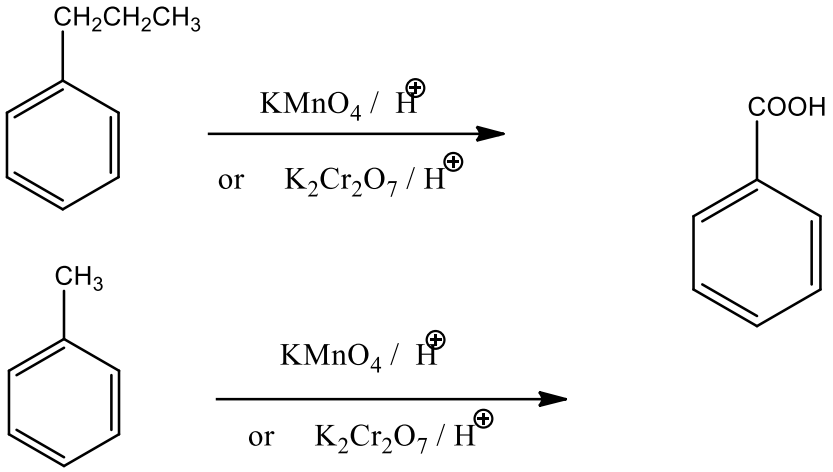
5. By the hydrolysis of 1,1,1 tri halides with alkali



6. By the reaction of alkene with carbon monoxide and steam

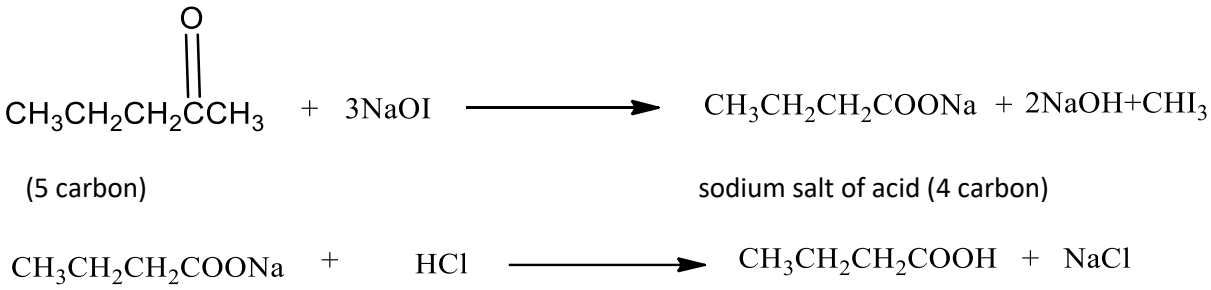


6. By the oxidation of alkylbenzene



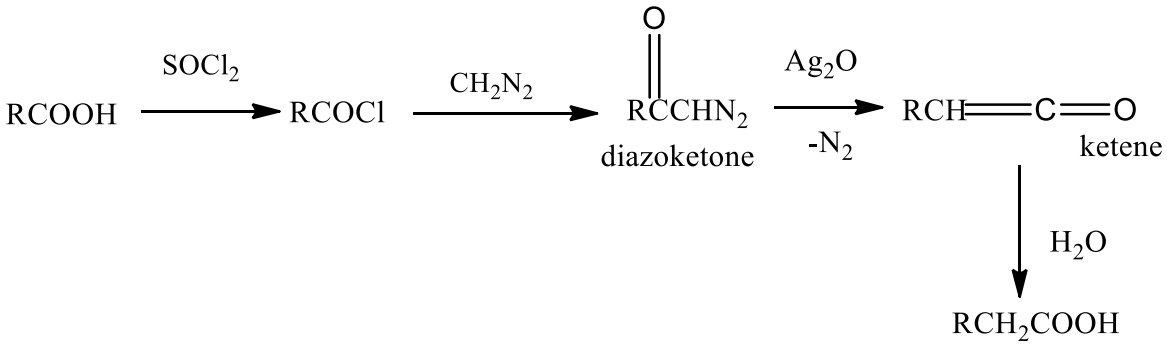
In this oxidation, product does not depend on the length of the side chain. The product is benzoic acid.

7. By the oxidation of methyl ketone with sodium hypohalite



The carboxylic acid has one carbon atom less than the parent ketone.

8. Arndt- Eistert synthesis (for increasing the chain length by - CH2-)

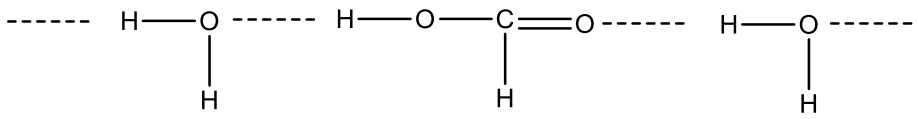


diazoketone formed undergoes **Wolff rearrangement** to form ketene.

PHYSICAL PROPERTIES

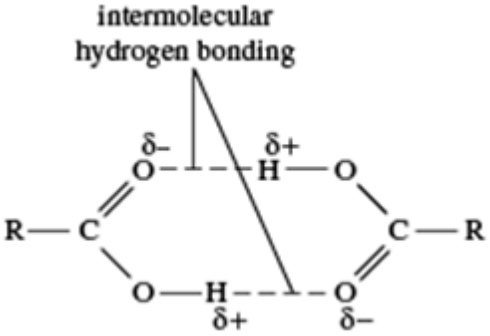
1. Lower aliphatic acids are pungent smelling liquids whereas higher aliphatic acids(higher than C-10) are odourless solids.

2. The first four members are very soluble in water, and the solubility decreases as molecular weight increases . The solubility of acids are due to the formation of H- bonds with water . As the molecular weight increases the hydrocarbon part (alkyl group) become larger which resist the formation of H-bonds with water molecules.



H - BONDING

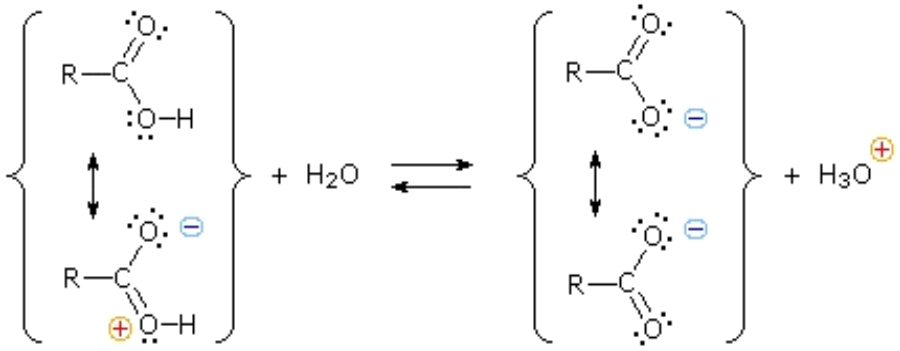
3. Carboxylic acids have much higher boiling point than expected from their molecular weight. This can be explained by H-bonding. The acids exist as cyclic dimers . (8 membered ring present)



cyclic dimer of acid

4.Melting point of aliphatic carboxylic acids do not show a regular pattern. The melting point of an acid containing even number carbon atoms is higher than that of the odd acid immediately below and above it in homologous series.

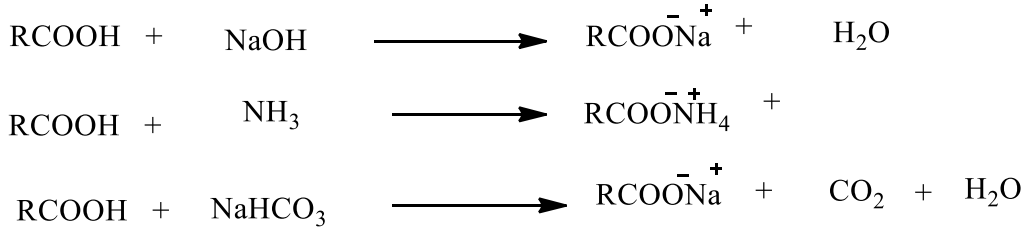
5.The acidity of carboxylic acid is due to resonance stabilization of its anion.(carboxylate ion)



resonating structures of carboxylic acid and caboxylate ion

REACTIONS OF CARBOXYLIC ACIDS

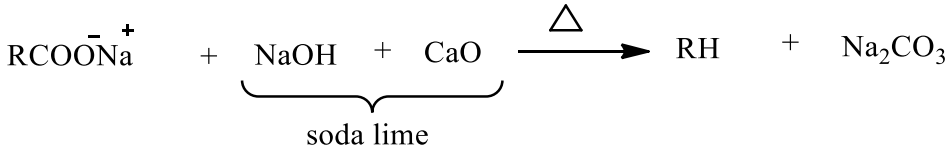
1. Salt formation-



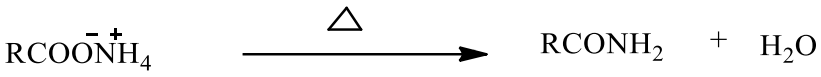
Reaction of carboxylic acid with aqueous **$NaHCO_3$** is chemical test for the detection of **-COOH** group.

The salts of carboxylic acids are important for the synthesis of following class of compounds:

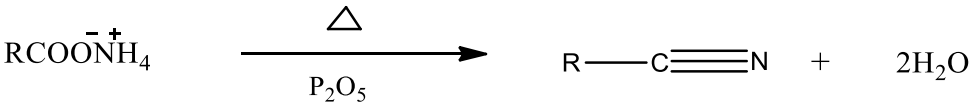
(a) Hydrocarbon



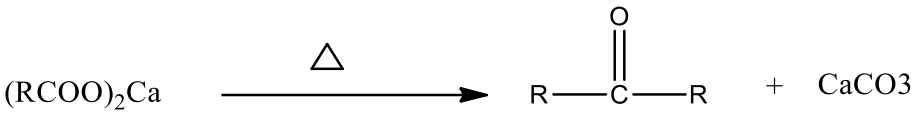
(b) amides



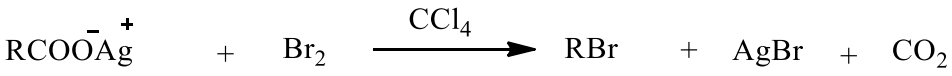
(c) alkyl nitriles



(d) ketones

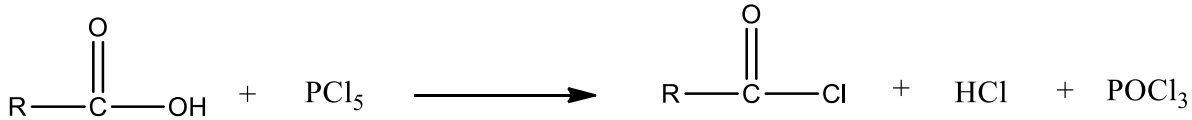


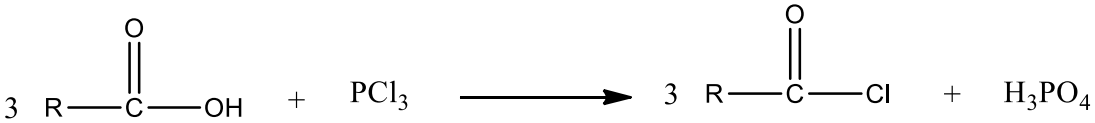
(e)alkyl halides

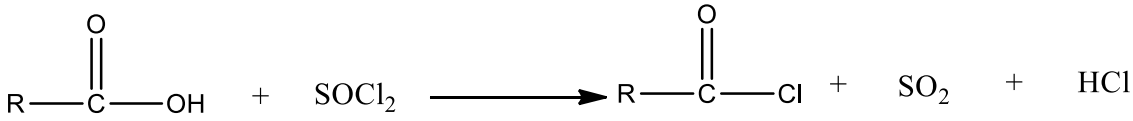


Synthesis of primary alkyl halides by the reaction of carboxylic acid and bromine in CCl_4 is **Hunsdiecker reaction.**

2.Conversion of acid to acid halide

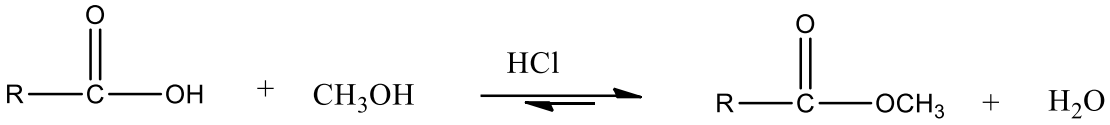




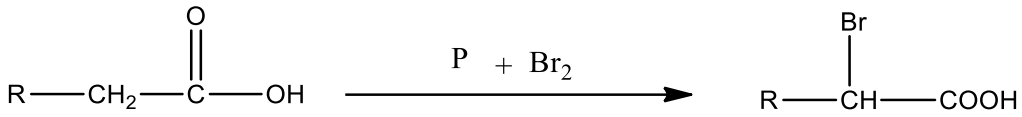


3. Conversion of acid to esters

The reaction of carboxylic acid with alcohol in the presence of an acid catalyst to form an ester is known as **Fischer esterification**



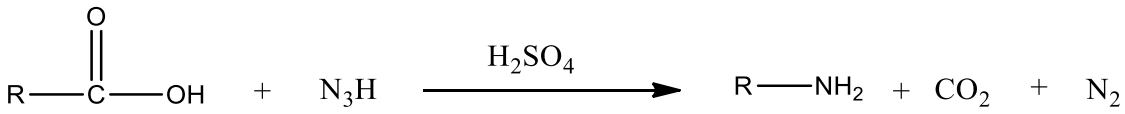
4.Halogenation of the α- carbon of carboxylic acid



This reaction is known as **Hell-Volhard -Zelinsky reactiion (HVZ)** , it has wide synthetic importance.

5. Conversion of acid to primary amines

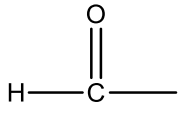
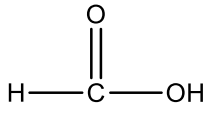
Reaction of carboxylic acid with hydrazoic acid (N_3H) in presence of H_2SO_4 leads to the formation of primary amine containing **one carbon atom less** than the parent acid. This reaction is known as **Schmidt reaction.**



6. . Conversion of acid to primary alcohol

Reduction is carried out by hydride transfer. $LiAlH_4$ is hydride donor.

FORMIC ACID:

- Formic acid is the only acid that reduces Fehling solution as well as Tollen's reagent.
- due to the presence of  group in formic acid 
- It does not give H.V.Z. reaction .(lack of α- hydrogen)