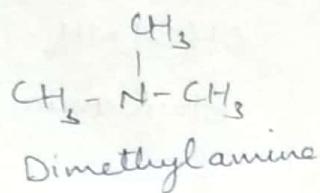
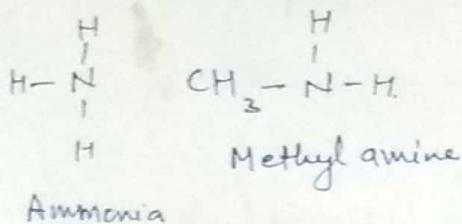


Aliphatic Amines

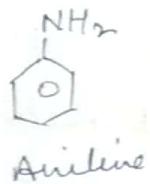
(3)

Amines are derivative of ammonia (NH_3) in which one or more hydrogen atoms are replaced by alkyl groups.

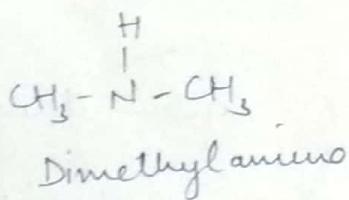


Amines are broadly of two types:-

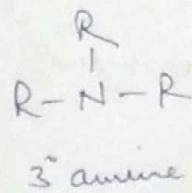
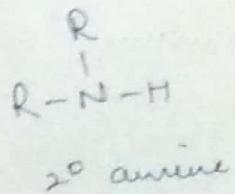
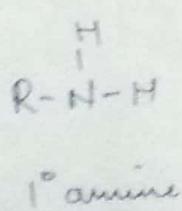
a) Aromatic amines :- These are amines in which ^{at least} one hydrogen is replaced by aromatic gp.



b) Aliphatic amines :- These are amines in which ~~at least one~~ hydrogens are replaced by aliphatic gps.

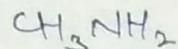


Amines can also be classified as 1° , 2° & 3° according to number of alkyl groups attached to N atoms

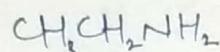


NOMENCLATURE OF AMINES:-

1) COMMON SYSTEM:- In common system, they are named as 'Alkylamine'. The name is written as one word.

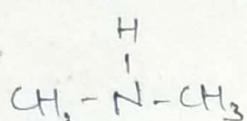


Methyl amine

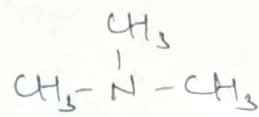


Ethylamine

* When 2 or 3 identical alkyl groups are attached to Nitrogen atom, prefix Di or Tri- is added to name of amine

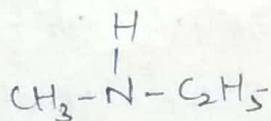


Dimethylamine



Trimethylamine

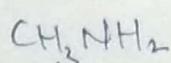
* When 2 or 3 different alkyl groups are attached to Nitrogen atom, they are named in alphabetic order.



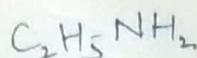
Ethylmethylamine

2) IUPAC SYSTEM:- In IUPAC system, they are named as

'Alkanamine'. If necessary a number is added to indicate position of $-\text{NH}_2$ gp.



Methanamine

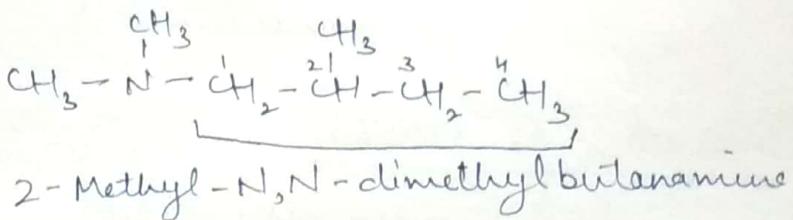
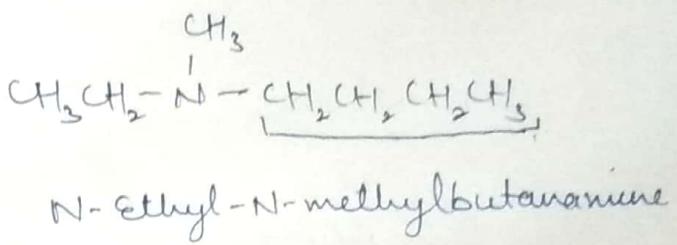
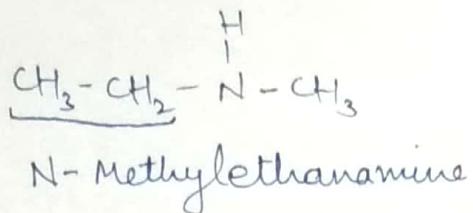


Ethanamine



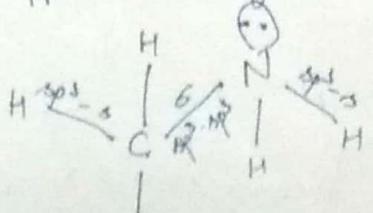
2-propanamine

* 2° or 3° amines are named as N-substituted derivative of 1° amine. The largest group attached to N atom is chosen as parent organic gp of 1° amine. Remaining alkyl gp are named as substituent by using prefix N- to indicate that they are attached to Nitrogen.

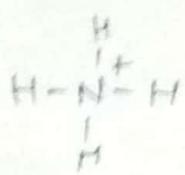


STRUCTURE OF AMINES :- Eg. CH_3NH_2

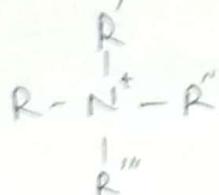
In methylamine, both N and C are sp^3 hybridized. One of the sp^3 orbital of Nitrogen is completely filled and can't take part in bond formation. The C-N σ bond is formed by overlap of sp^3 orbital of C and N. Each N-H σ bond is formed by overlap of sp^3 orbital of N and s orbital of H. C-H σ bond is formed by overlap of sp^3 orbital of C and s orbital of H. Amines like ammonia are pyramidal in shape with bond angle approximately 108° .



Salt of amines:- All amines are basic and they react with acid to form salt. The salt is related to ammonium salt (NH_4^+) in which all 4 hydrogens are replaced by alkyl groups. Such compound is called Quaternary ammonium salt. Salts of amine are soluble in water.



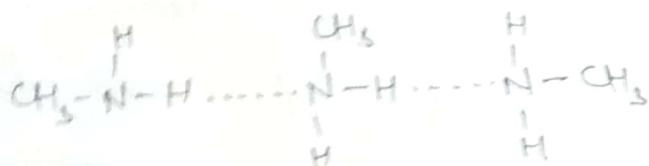
Ammonium ion



Quaternary Ammonium salt

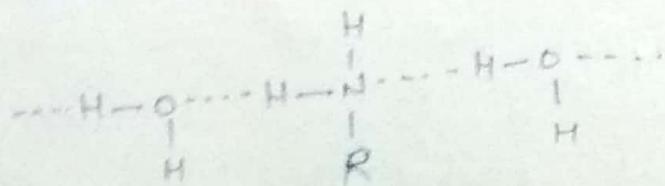
PHYSICAL PROPERTIES OF AMINES

- i) Amines are polar compounds. Except 3° amines, other amines can form intermolecular H-bonds.



∴ Amines have higher boiling point than non-polar compounds of similar mol. wt.

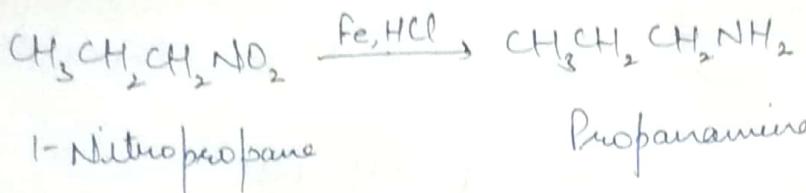
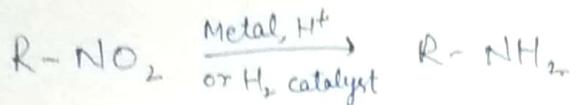
- ② Amines (upto 6 C atoms) are soluble in H_2O ∵ they are capable of forming H-bonds with H_2O . Amines are also soluble in benzene and other



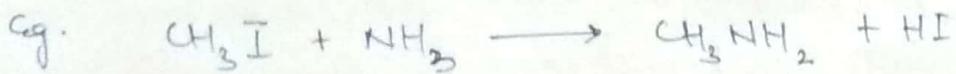
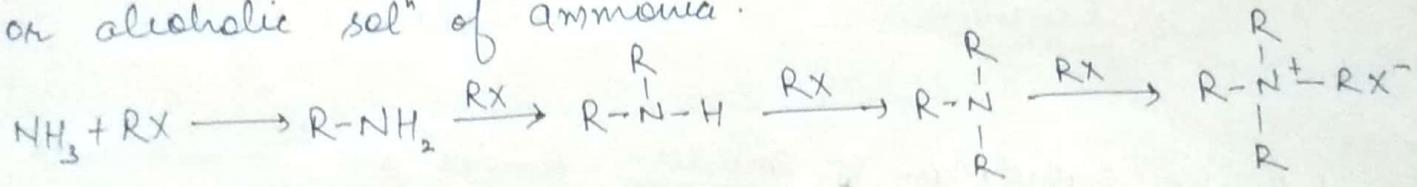
- ③ Amines have characteristic ammonia like smell.
 ④ Lower amines are gases or low boiling pt. liquids

PREPARATION OF AMINES

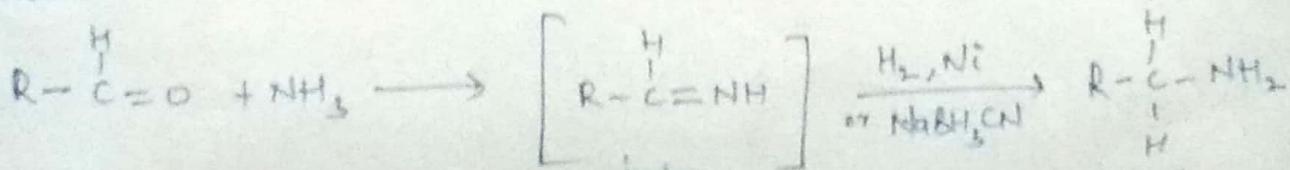
1) Reduction of Nitrocompounds: Amines can be produced by reduction of nitro compounds either by catalytic hydrogenation using molecular hydrogen or by chemical reduction with metal + acid.

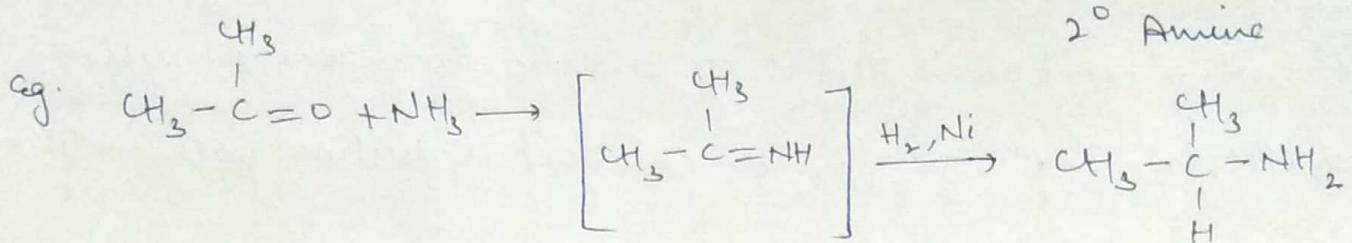
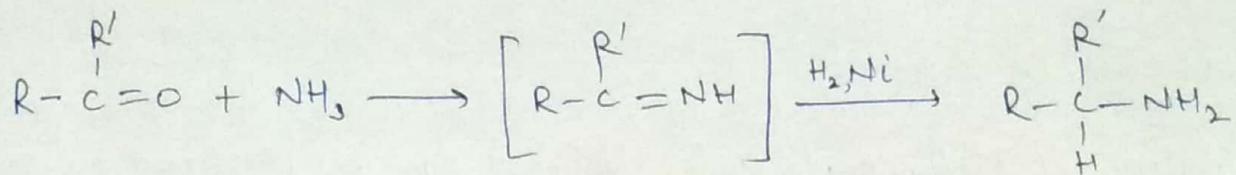


2) Reaction of halide with ammonia or amine: Many organic halogen compounds are converted into amines by treatment with ag. or alcoholic sol" of ammonia.

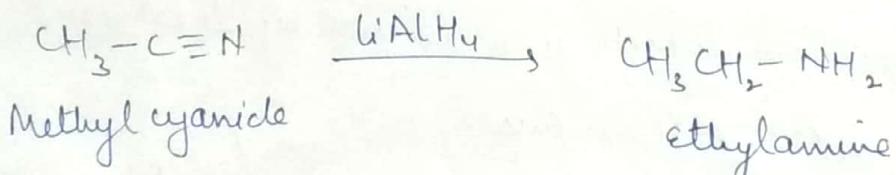
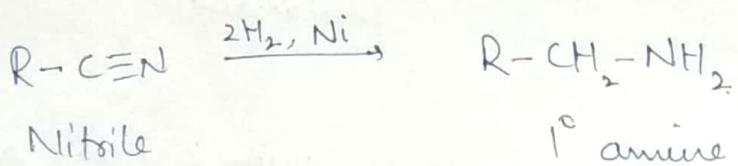


3) Reductive Amination: Aldehydes and ketones are converted into amines by reductive amination i.e. reduction in presence of ammonia.

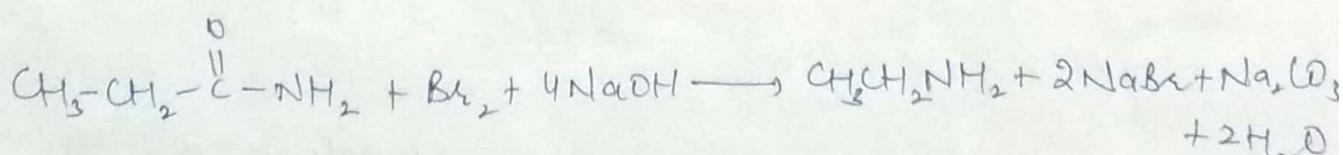
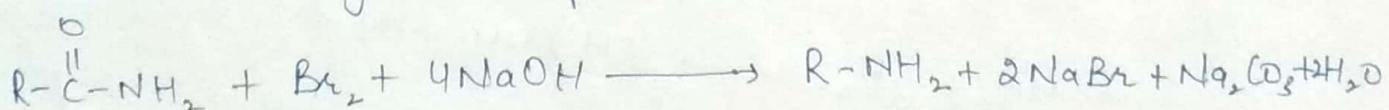




4) Reduction of Nitriles: Amines can be prepared by reduction of nitriles (alkyl cyanide) with $H_2 + Ni$ or lithium aluminium hydride

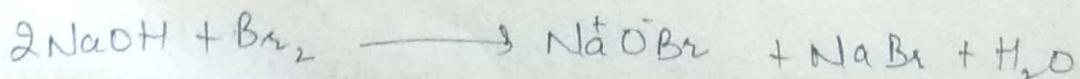


5) Hofmann degradation of Amides: Amides are warmed with Bromine and conc. aq. NaOH solⁿ. The product contains one C less than original compound.

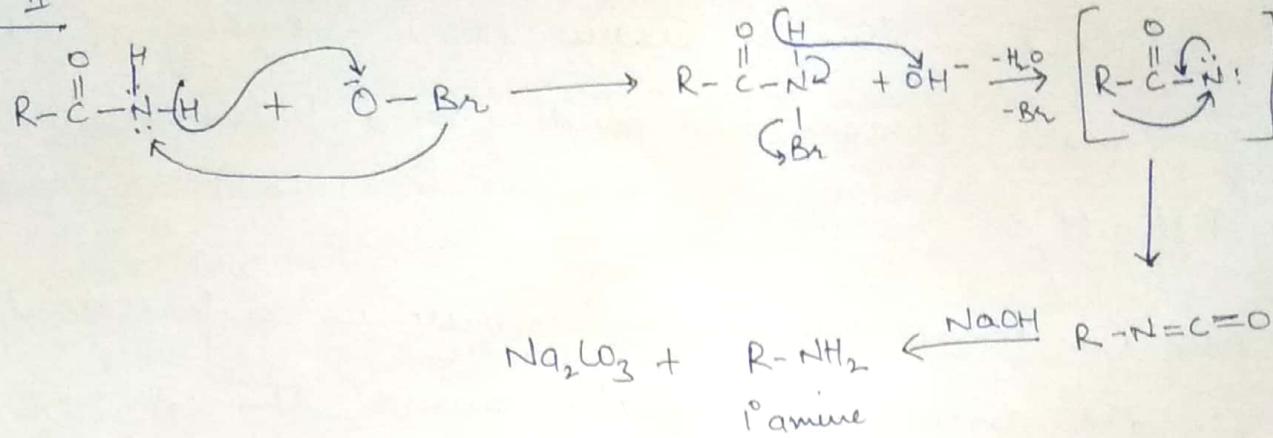


Mechanism:

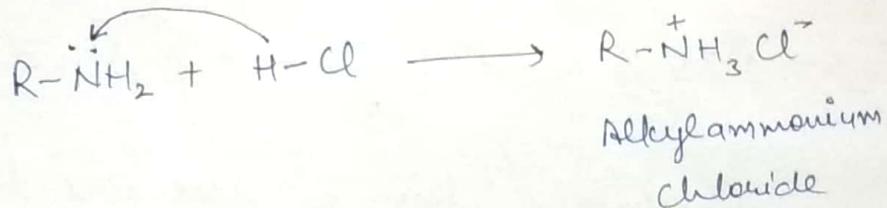
Step-I Formation of attacking species:



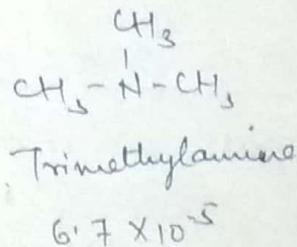
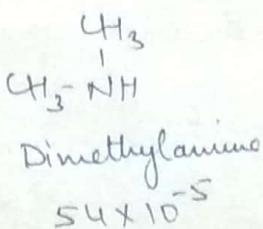
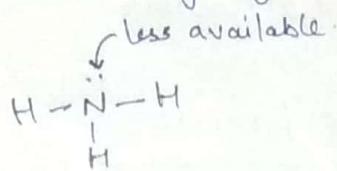
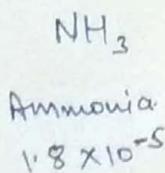
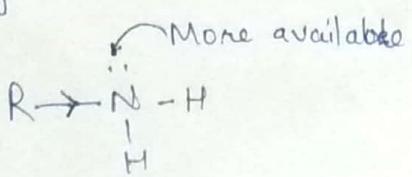
Step-II



BASICITY OF AMINES:- Amines are basic in nature. This is because they possess an unshared pair of electrons on nitrogen. This lone pair of \bar{e} is available for the formation of new bond with H^+ or lewis acid. These amines react with acid to form salt



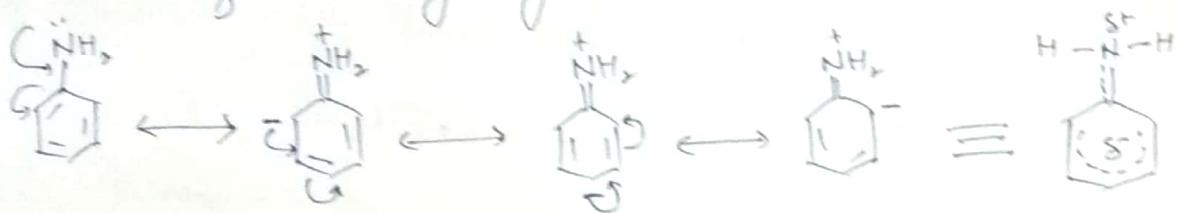
Aliphatic amines are stronger base than NH_3 . This is \because alkyl groups are \bar{e} releasing. They \uparrow e the electron density around Nitrogen and thus \uparrow e the availability of lone pair of electrons.



Greater the number of \bar{e} releasing alkyl groups, the greater the availability of nitrogen's lone pair and stronger the base. But trimethylamine is weaker base than dimethylamine and

methylamine. This is because steric crowding of 3 methyl groups make approach and bonding by a proton relatively difficult.

Aromatic amines are much less basic in comparison to aliphatic amines. In aliphatic amines, the non bonding electron pair on N atom is localized and fully available for co-ordination with H^+ . On the other hand, in aromatic amines, the non bonding $\bar{\epsilon}$ pair is delocalized into benzene ring by resonance.

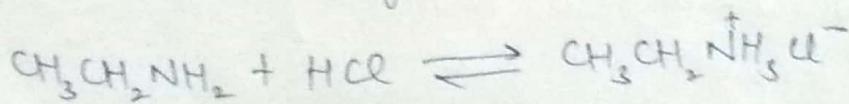


The non bonding $\bar{\epsilon}$ pair in resonance hybrid is dispersed over ~~before~~ benzene ring and is less available for protonation.

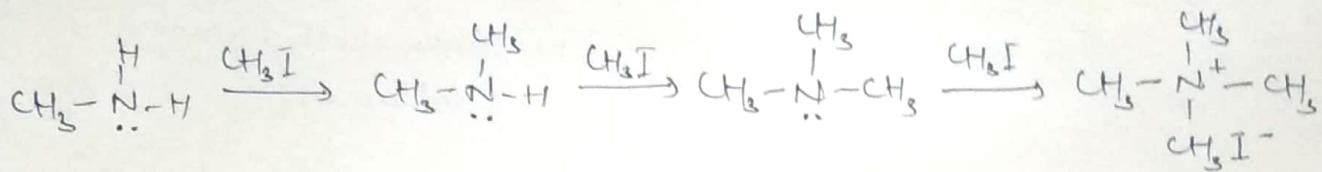
∴ Aromatic amines are less basic than aliphatic amines & show no resonance.

REACTIONS OF AMINES!

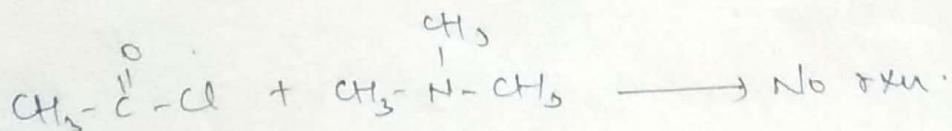
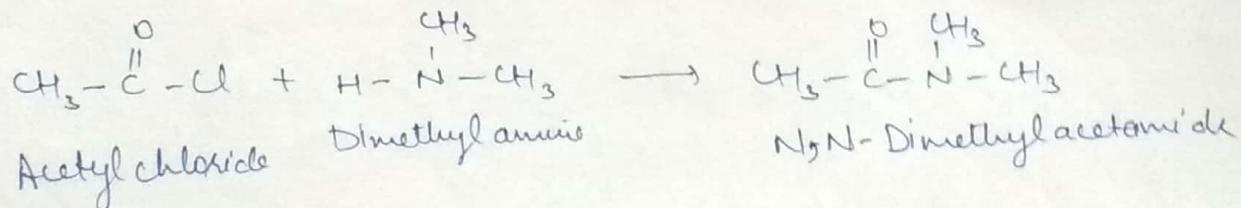
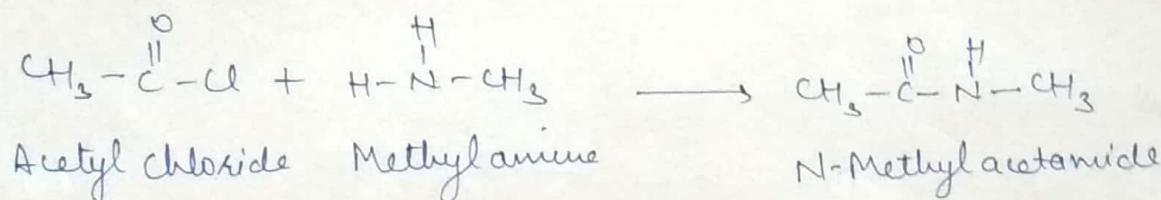
- 1) Salt formation :- Amines are basic compounds. They react with mineral acid to form salt.



Reaction with alkyl halide:- When treated with excess of alkyl halide, hydrogen atom attached to N are replaced successively by alkyl groups to give quaternary ammonium salt as final product.



3) Reaction with Acid chlorides: Amines react with acid chlorides to give amides. 1° amine gives N-substituted amide
 2° amine " N,N-Disubstituted amide
 3° amine does not react



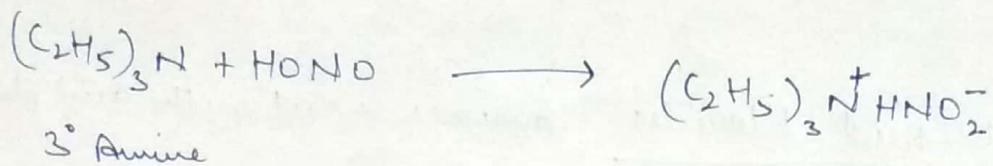
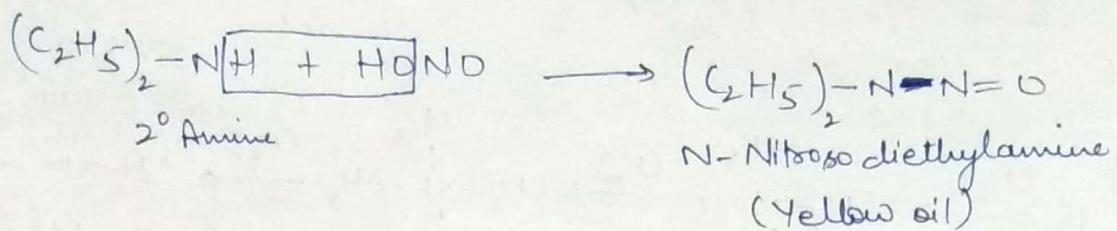
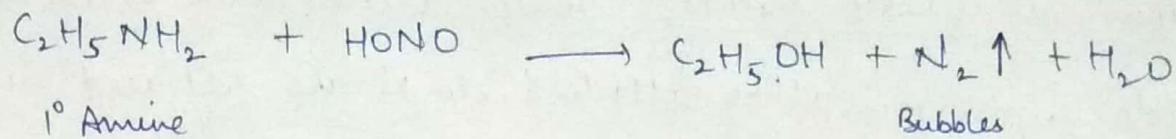
TEST FOR QUALITATIVE IDENTIFICATION OF 1° , 2° & 3° Amines:

4) Reaction with nitrous acid:- On rxn with HNO_2 ,

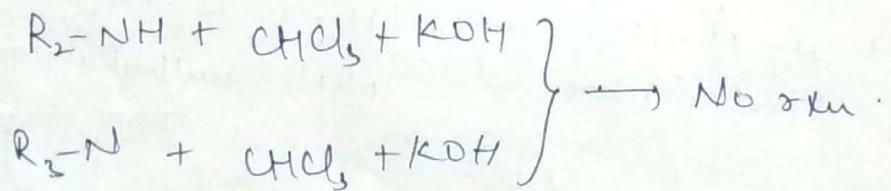
1° amine gives alcohol and N_2 gas

2° " " Nitrosoamines (H_2O insoluble Yellow oil)

3° " " Trialkylammonium nitrate salt (H_2O soluble)



5) Coubylamine test or isocyanide test: - 1° amines react with KOH in ethanol to form isocyanide \Leftrightarrow have very offensive smell.
 2° and 3° amines doesn't give this test.

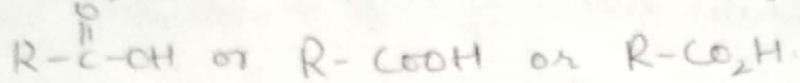


X

①

Carboxylic acids:

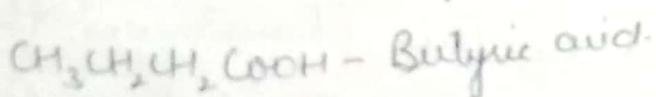
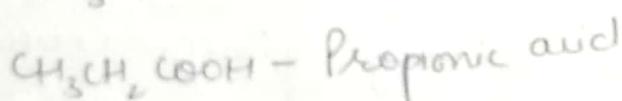
These are the organic compounds which contain $-COOH$ (carboxyl) functional group. They have general formula:



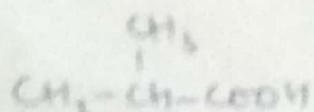
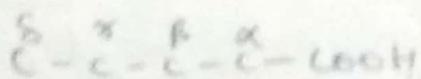
where R = alkyl group.

Nomenclature: There are 3 ways for their nomenclature:

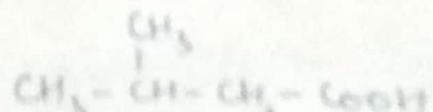
a) Common system: The common names are usually derived from latin or greek words that indicate original source of acid. They don't follow any rule except that all common names of acids end in -ic acid.



Greek letters $\alpha, \beta, \gamma, \delta$ etc. are used to indicate the position of substituent

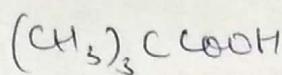


α -methyl propionic acid

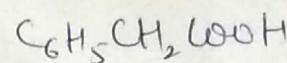


β -methyl butyric acid

b) Derived system- Some carboxylic acids may be named as substituted acetic acids.

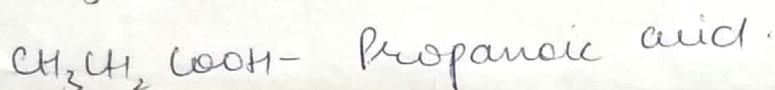
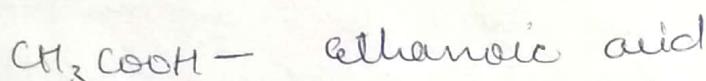


Trimethylacetic acid

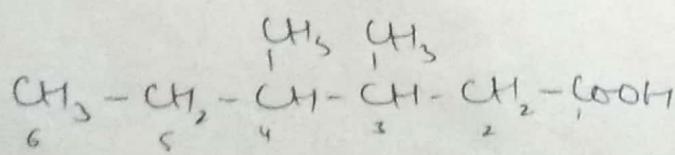
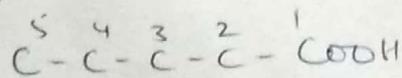


Phenylacetic acid.

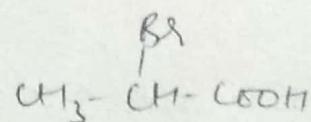
c) IUPAC system- In the IUPAC system, the carboxylic acids are named as alkanic acids. The systemic name of individual acid is obtained by replacing the ending '-e' of corresponding alkane by '-oic acid'.



for naming higher members, the longest continuous chain containing the carbonyl group (-COOH) is selected. The no. of carbons in this chain gives the name of parent alkane. The position of substituent is indicated by the numbers. The carbonyl carbon is always given number 1.



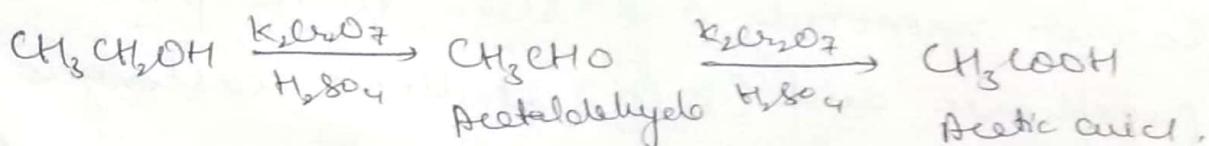
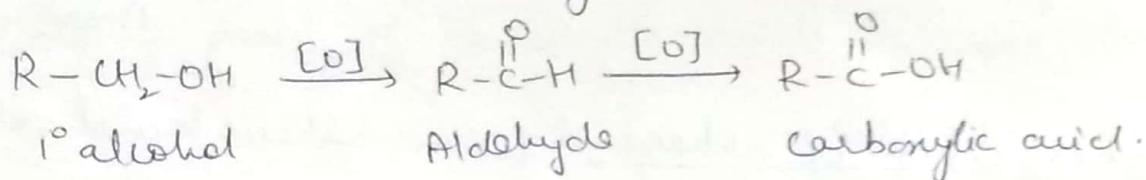
3,4-Dimethylhexanoic acid



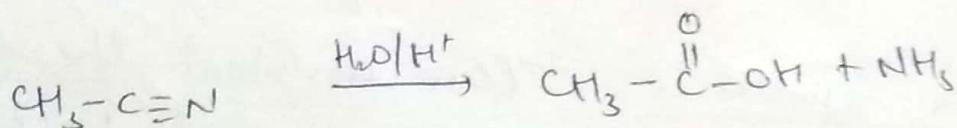
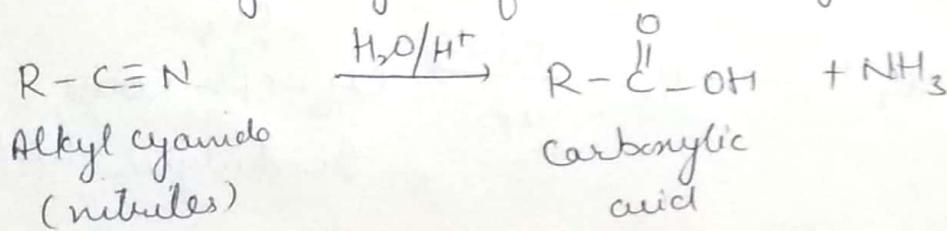
2-Bromopropanoic acid

Method of Preparation:-

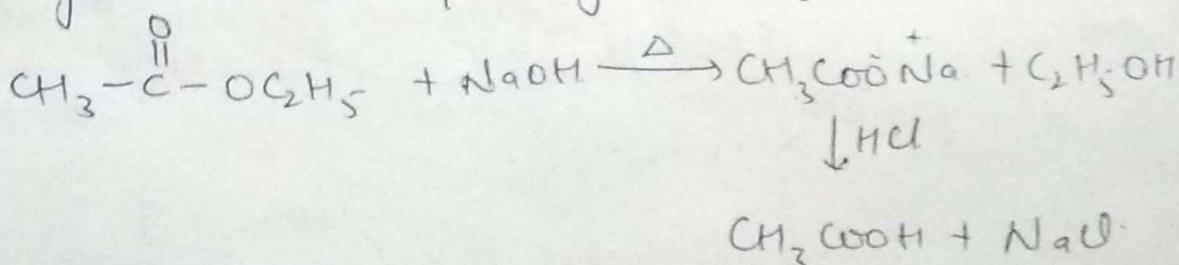
i) Oxidation of 1° alcohols or aldehydes :- 1° ~~alcohols~~ alcohols or aldehydes undergo oxidation with a mixture of Potassium dichromate or sulfuric acid to form carboxylic acids. The alcohols are first oxidised to aldehydes and then to a carboxylic acid.



ii) Hydrolysis of Nitriles or alkyl cyanides The nitriles on acid hydrolysis form carboxylic acids.

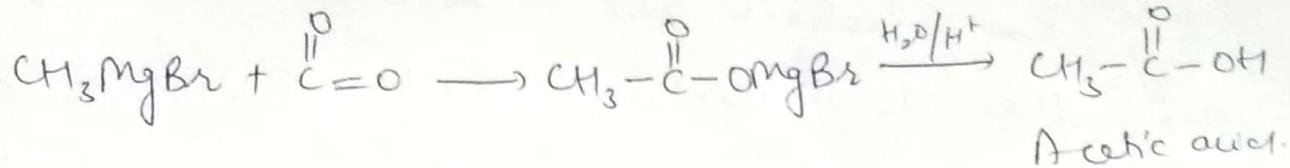
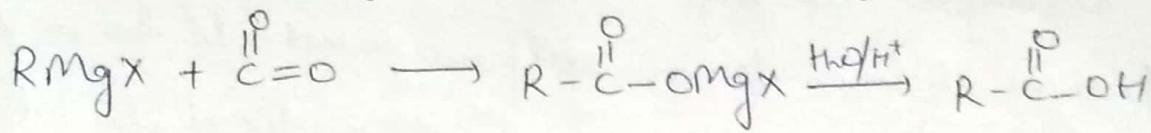


(iii) Hydrolysis of Esters:- When an ester is boiled in conc. NaOH , sodium salt of acid is formed. This on titration with dil. HCl gives the corresponding carboxylic acid.

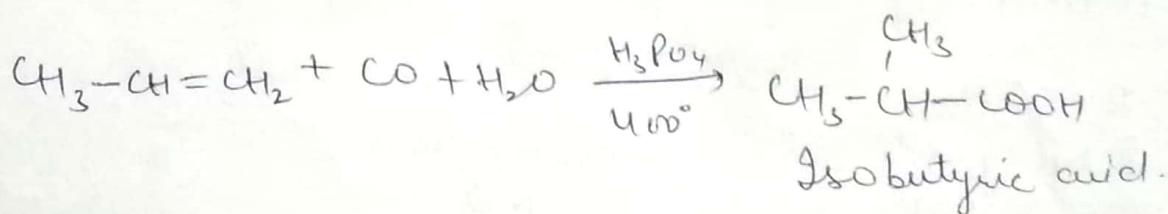
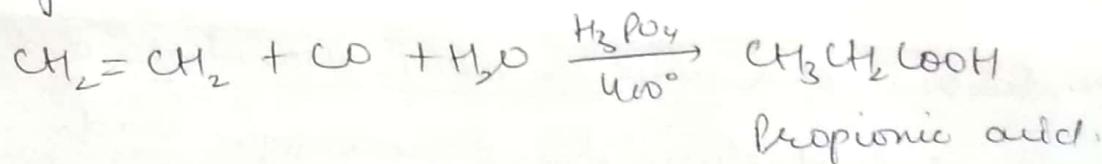


(4)

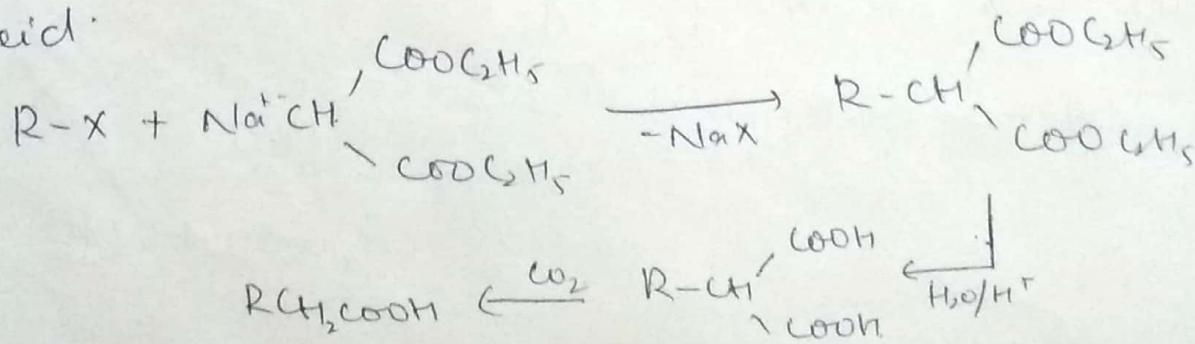
iv) Reaction of Grignard reagents with CO_2 : Grignard reagent react with carbon dioxide to form addition product that can be hydrolysed to carboxylic acids.



v) Carbonylation of alkenes: When alkene is heated with carbon monoxide and steam under pressure with phosphoric acid (H_3PO_4) at 400°C , carboxylic acid are formed. This is also called Koch reaction.



vi) Malonic ester synthesis: This involves the reaction of an alkyl halide with sodium derivative of diethyl malonate to give a substituted malonic ester. This can be hydrolysed and decarboxylated to yield an acid.



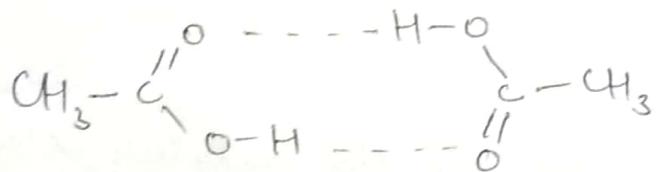
(5)

Physical Properties:-

- (1) lower carboxylic acids (upto 4_o) are liquids & sharp and disagreeable odors. Higher members are waxlike and odorless.
- (2) Boiling point rises regularly & \propto to molecular wt.
- (3) melting point rises irregularly & \propto to mol. wt.
- (4) Boiling point of carboxylic acids ~~are~~ are higher than those of alcohols of same molecular weight.

	Mol wt	B.Pt
CH ₃ COOH	60	118
CH ₃ CH ₂ CH ₂ OH	60	97

This is due to hydrogen bonding b/w acid molecules.

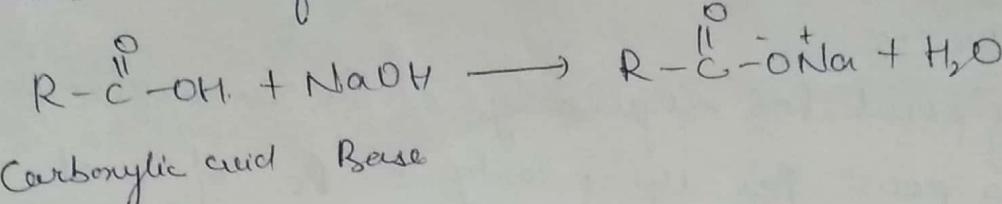


- (5) First four members are completely soluble in H₂O. This is due to ability of carbonyl gp to form H-bonding with H₂O molecules. As the hydrocarbon chain in acid lengthens, the solubility of acid in water falls off rapidly.

Acidity of carboxylic acids:

(6)

Carboxylic acids are acidic in nature. They can donate a proton and form salts with bases.



Acidity constant :- Strong acids completely ionise in aq. solution. Carboxylic acids are weak acids. They are only partially ionized in aq. solution and \rightleftharpoons exist b/w ionized and unionized form.

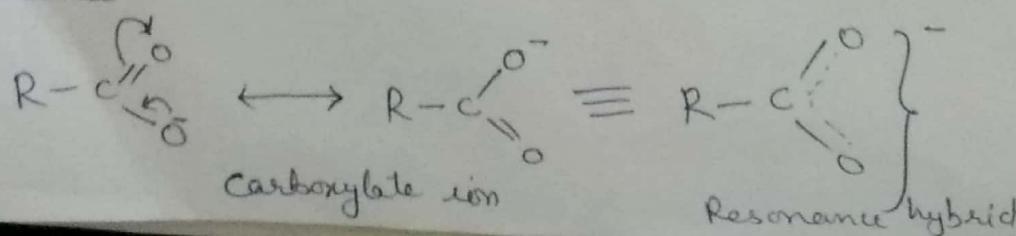


The extent of ionization is described by an \rightleftharpoons constant K_a , ~~is~~ known as acidity constant.

$$K_a = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]}$$

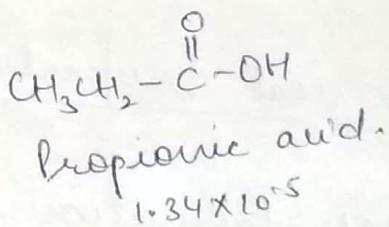
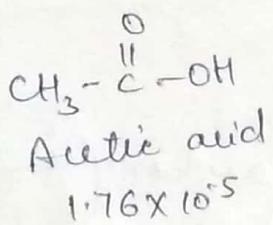
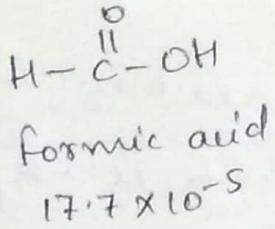
The acidity constant describes the relative strength of a weak acid. Stronger acid will have higher numerical value of acidity constant.

Explanation of acidity :- Carboxylic acids are acidic and lose a proton readily \therefore the carboxylate ion formed by ionization or reaction \in a base is stabilized by resonance.



The stability of carbonylate ion can be also explained on the basis of its molecular orbital structure. The carbon atom of carbonylate ion is sp^2 -hybridized. It is bound to each oxygen by a σ bond. The unused carbon p-orbital overlaps with p-orbitals of both oxygen atoms to form stable delocalised molecular orbital.

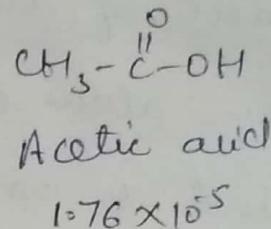
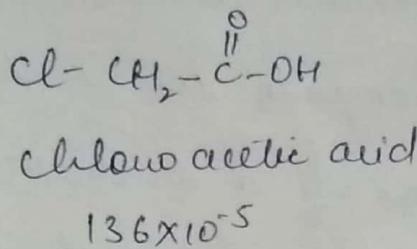
Effect of substituent on acidity:- The most important factor affecting the acidity is the inductive effect of substituent on the α -carbon atom. electron releasing alkyl group less the acidity. This is \therefore the $\bar{\epsilon}$ releasing groups \uparrow the -ve charge on carbonylate ion and destabilize it. The loss of proton becomes more difficult. As the size of alkyl group \uparrow , the acidity \downarrow .



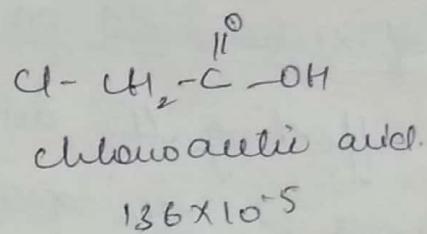
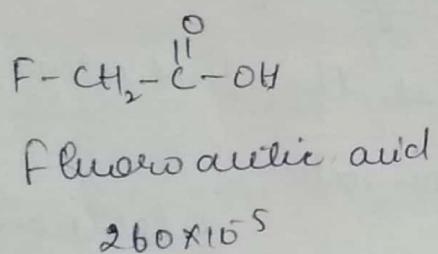
electron withdrawing substituent \uparrow the acidity \uparrow this is \therefore electron withdrawing substituent \therefore the negative charge on the carbonylate ion and stabilize it. The loss of proton becomes relatively easy.

(8)

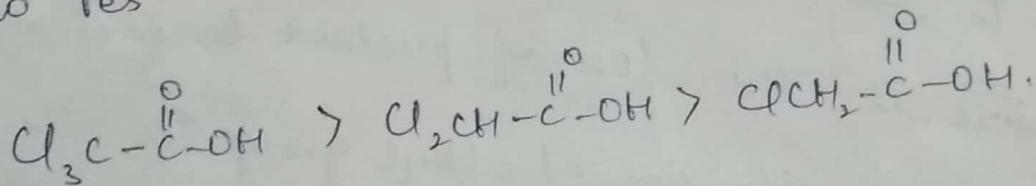
Chloroacetic acid is about 100 times stronger than acetic acid.



The strong electron withdrawing group \uparrow s acidity of carboxylic acid.

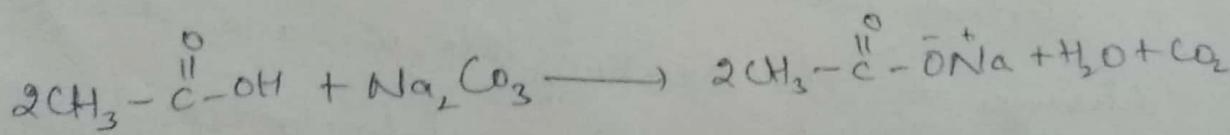
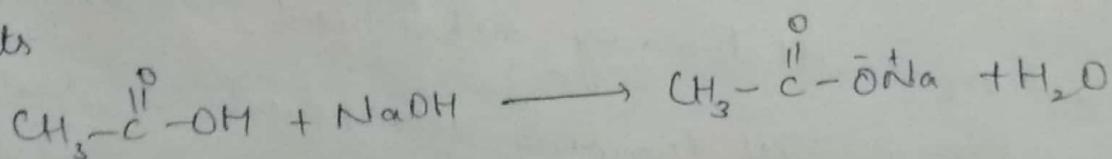


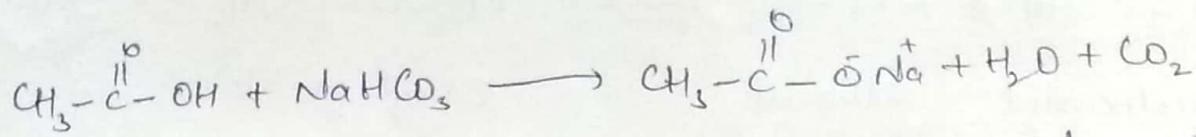
As the number of $\bar{\epsilon}$ electrons withdrawing substituent \uparrow s, acidity also \uparrow s.



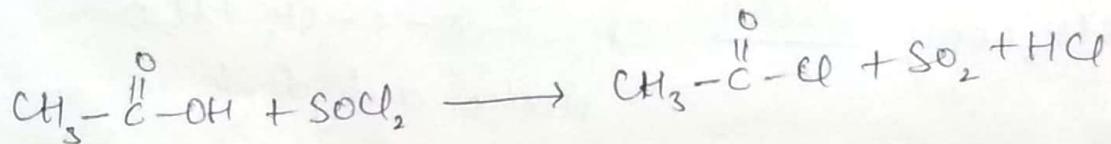
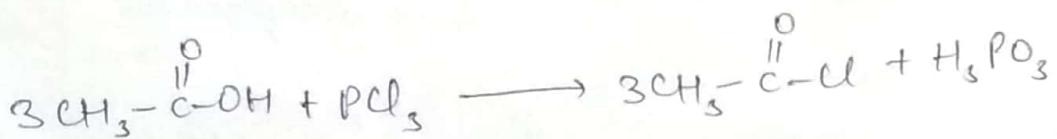
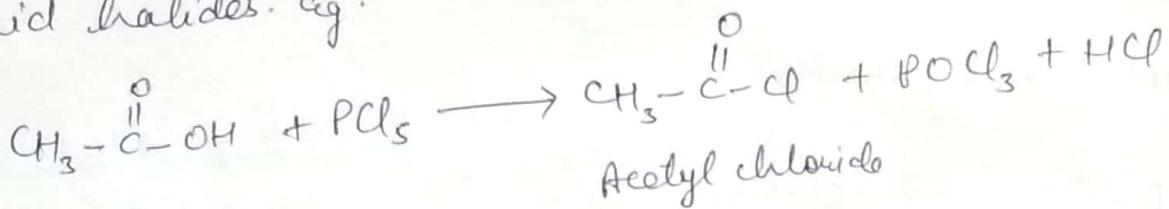
Chemical properties :-

i) Salt formation: Carboxylic acids react with hydroxides carbonates and bicarbonates to form corresponding salts

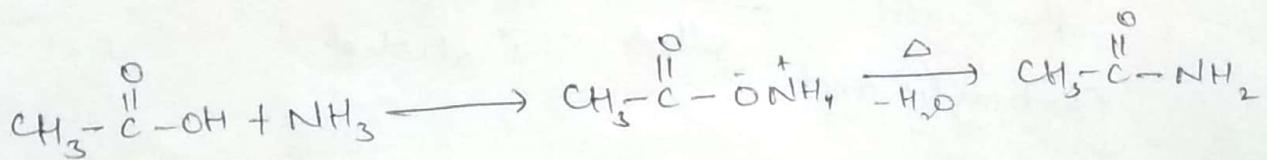
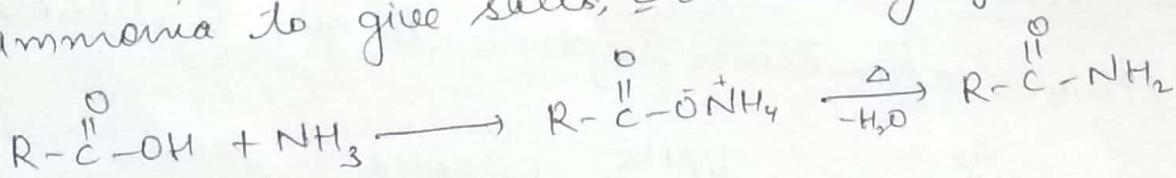




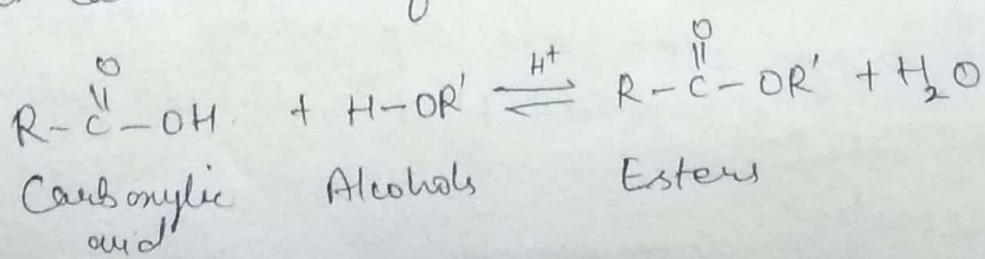
ii) Formation of acid halides: Carbonylic acid react with phosphorous halides or thionyl chloride (SOCl_2) to form acid halides. e.g.

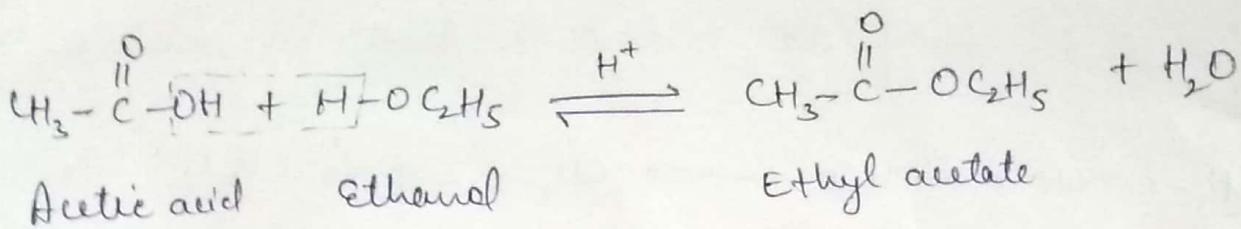


iii) Formation of amides: Carbonylic acids react with ammonia to give salts, & on heating yield amides.

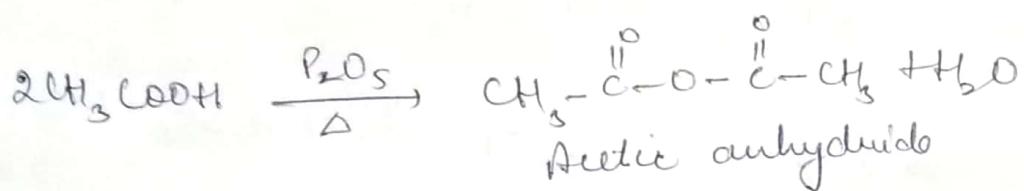
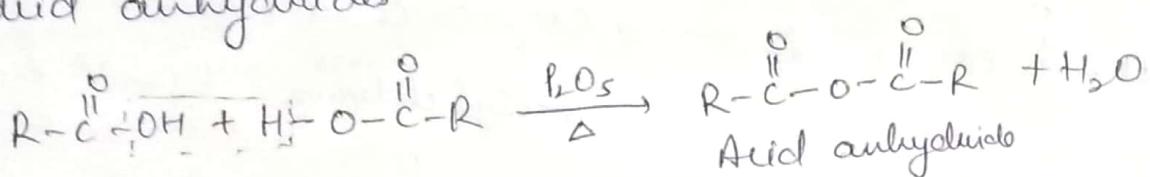


iv) Formation of esters: Carbonylic acids react with alcohol in the presence of a strong acid catalyst to form esters. The reaction is reversible and is called esterification.

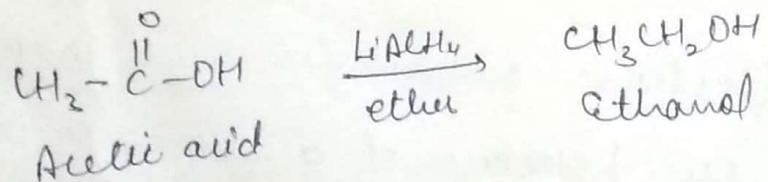
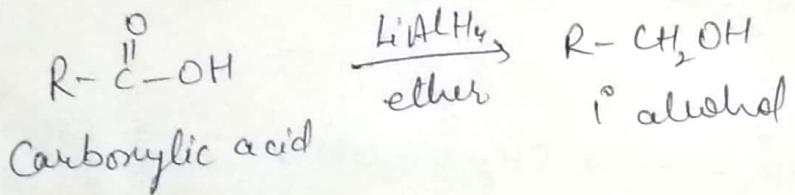




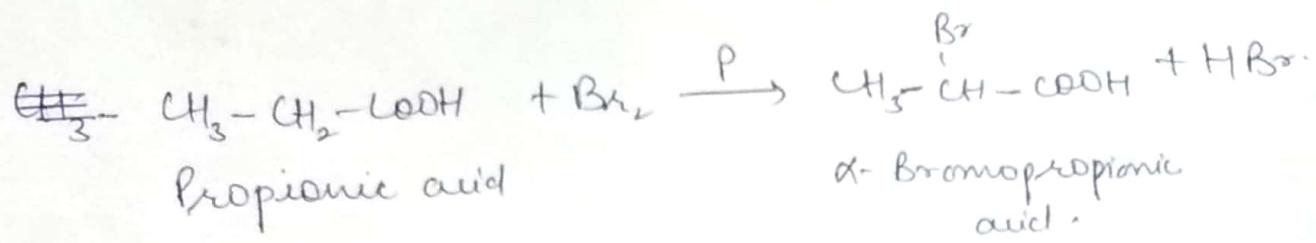
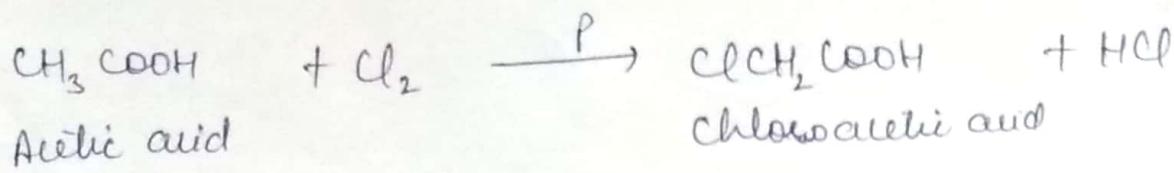
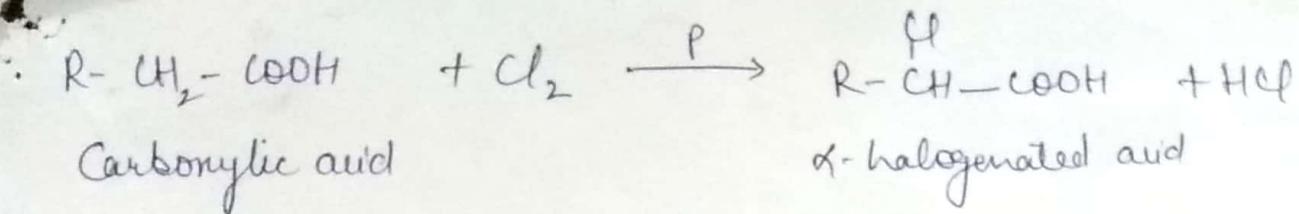
v) Formation of anhydrides: Carbonylic acids undergo dehydration \bar{c} phosphorus pentoxide (P_2O_5) to form acid anhydrides.



vi) Reduction: Carbonylic acids undergo reduction \bar{c} lithium aluminium hydride to give ${}^{\circ}$ alcohols.



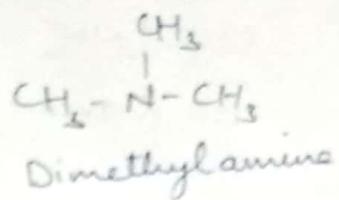
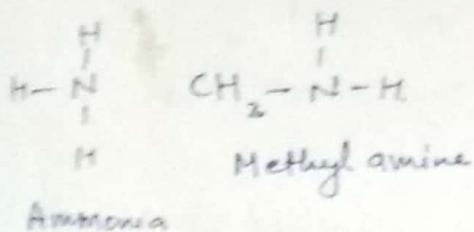
vii) α -Halogenation: When a carbonylic acid that contains α -hydrogen is t/t \bar{c} Cl_2 or Br_2 in presence of phosphorus, the α -hydrogen atom are replaced by Cl or Br atom. This rxn is also called Hell-Volhard-Zelinsky (HVZ) reaction.



Aliphatic Amines

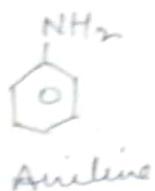
(5)

Amines are derivatives of ammonia (NH_3) in which one or more hydrogen atoms are replaced by alkyl groups.



Amines are broadly of two types:-

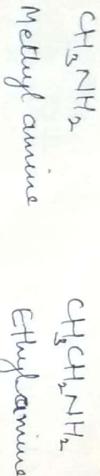
a) Aromatic amines :- These are amines in which ^{at least} one hydrogen is replaced by aromatic gp.



amine is... at least one

NOMENCLATURE OF AMINES:-

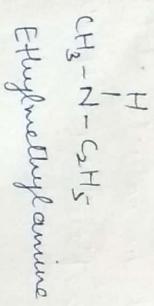
1) COMMON SYSTEM- In common system, they are named as 'Alkylamine'. The name is written as one word.



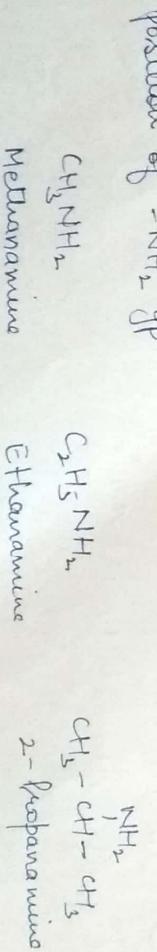
* When 2 or 3 identical alkyl groups are attached to Nitrogen atom, prefix Di or Tri- is added to name of amine



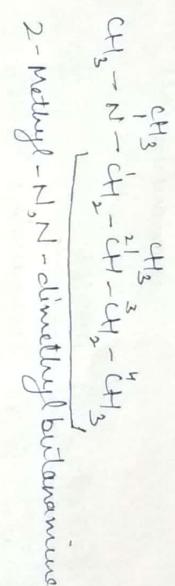
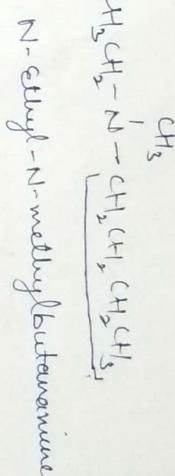
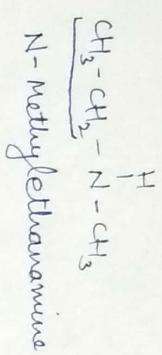
* When 2 or 3 different alkyl groups are attached to Nitrogen atom, they are named in alphabetic order.



2) IUPAC SYSTEM- In IUPAC system, they are named as 'Amines'. If necessary a number is added to indicate position of $-\text{NH}_2$ group.

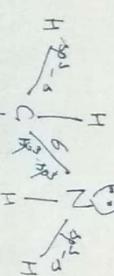


* 2° or 3° amines are named as N-substituted derivatives of 1° amine. The largest group attached to N atom is chosen as parent organic gp of 1° amine. Remaining alkyl gp are named as substituent by using prefix N- to indicate that they are attached to Nitrogen.



STRUCTURE OF AMINES :- eg: CH_3NH_2

In methylamine, both N and C are sp^3 hybridized. One of the sp^3 orbital of Nitrogen is completely filled and can't take part in bond formation. The C—N σ bond is formed by overlap of sp^3 orbital of C and N. Each N-H σ bond is formed by overlap of sp^3 orbital of N and s orbital of H. C—H σ bond is formed by overlap of sp^3 orbital of C and s orbital of H. Amines like ammonia are pyramidal in shape with bond angle approximately 108° .



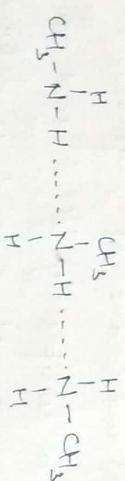
Salt of amines:- All amines are basic and they react with acid to form salt. The salt is related to ammonium salt (NH_4^+) in which all 4 hydrogens are replaced by alkyl groups. Such compound is called **Quaternary Ammonium Salt**. Salts of amine are soluble in water.



Ammonium ion
Quaternary Ammonium salt

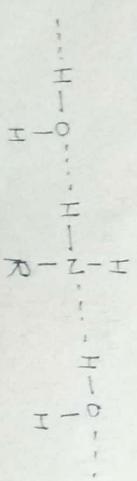
PHYSICAL PROPERTIES OF AMINES!

- 1) Amines are polar compounds. Except $\text{C}_6\text{H}_5\text{NH}_2$ amines, other amines can form intermolecular H-bonds.



- 2) Amines have higher boiling point than non-polar compounds of similar mol. wt.

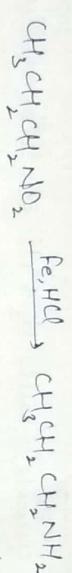
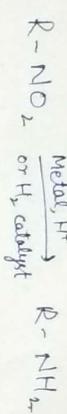
- 3) Amines (upto 6 C atoms) are soluble in H_2O : they are capable of forming H-bonds with H_2O . Amines are also soluble in benzene and other



- 4) Amines have characteristic ammonia like smell.
- 5) Lower amines are gases or low boiling pt. liquids

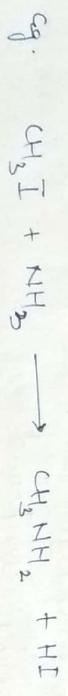
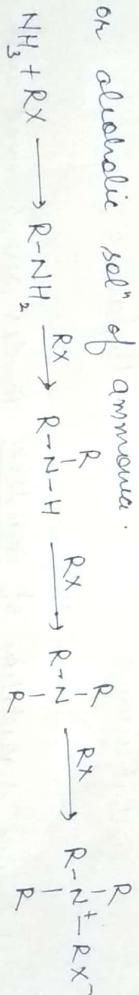
PREPARATION OF AMINES:

1) Reduction of Nitrocompounds! Amines can be produced by reduction of nitro compounds either by catalytic hydrogenation using molecular hydrogen or by chemical reduction with metal + acid.

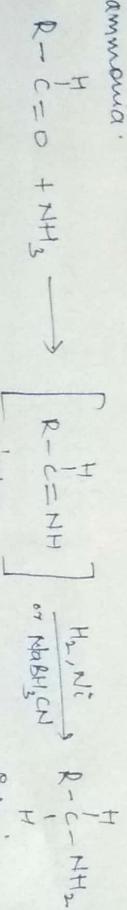


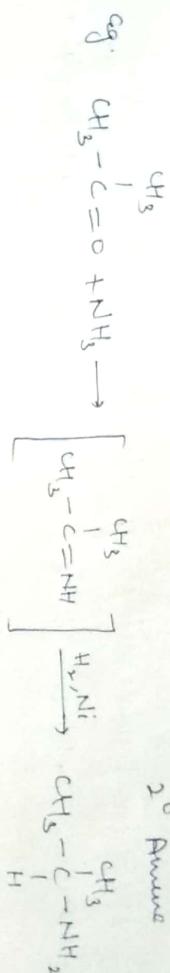
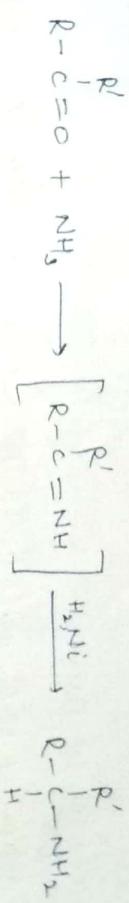
1-Nitropropane
Propanamine

2) Reaction of halide with ammonia or amine: Many organic halogen compounds are converted into amines by treatment with aq. or alcoholic soln of ammonia.

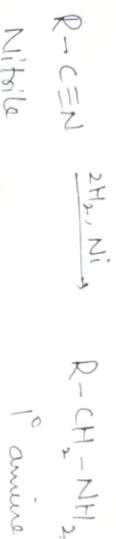


3) Reductive Amination: Aldehydes and ketones are converted into amines by reductive amination i.e. reduction in presence of ammonia.

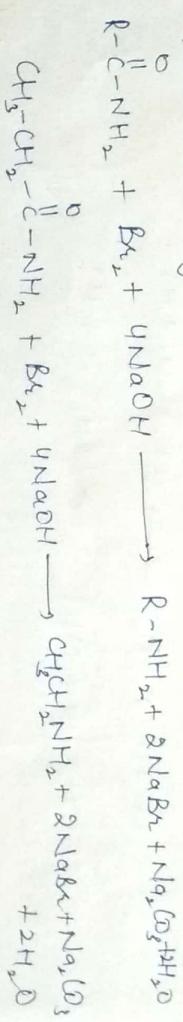




4) Reduction of Nitriles: Amines can be prepared by reduction of nitriles (alkyl cyanide) with H_2 & Ni or lithium aluminium hydride.

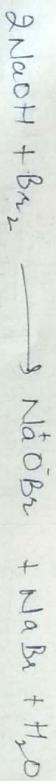


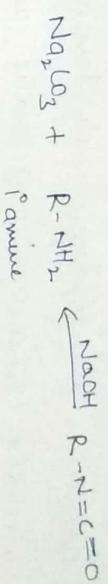
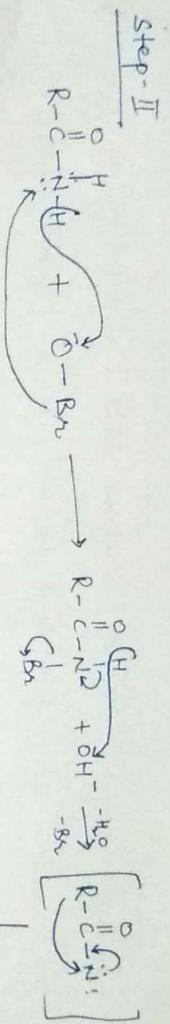
5) Hofmann degradation of Anilides: Anilides are warmed with Bu₄N⁺ and conc. aq. NaOH soln. The product contains one C less than original compound.



Mechanism:

Step-1: Formation of attacking species:-





BASICITY OF AMINES:- Amines are basic in nature. This is because they possess an unshared pair of electrons on nitrogen. Thus lone pair of e^- is available for the formation of new bond with H^+ or Lewis acid. Thus amines react with acid to form salt



Aliphatic amines are stronger base than NH_3 . This is because they are e^- releasing. They \uparrow the electron density around Nitrogen and thus \uparrow the availability of lone pair of electrons.

↑ More available ↓ Less available

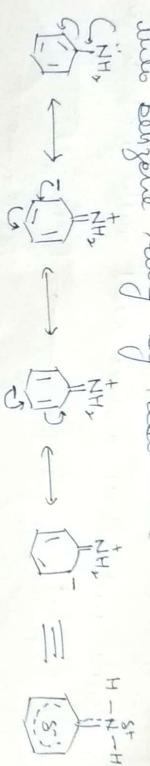


NH_3	CH_3-NH_2	$CH_3-\overset{\underset{\curvearrowleft}{H_3}}{N}-H$	$CH_3-\overset{\underset{\curvearrowleft}{H_3}}{N}-CH_3$
Ammonia 1.8×10^{-5}	Methylamine 3.7×10^{-5}	Dimethylamine 5.4×10^{-5}	Trimethylamine 6.7×10^{-5}

Greater the number of e^- releasing alkyl groups, the greater the availability of nitrogen lone pair and stronger the base. But trimethylamine is weaker base than dimethylamine and

methylamine. This is because steric crowding of 3 methyl groups make approach and bonding by a proton relatively difficult.

Aromatic amines are much less basic in comparison to aliphatic amines. In aliphatic amines, the non bonding electron pair on N atom is localized and fully available for co-ordination with H^+ . On the other hand, in aromatic amines, the non bonding e pair is delocalized into benzene ring by resonance.



The non bonding e pair in resonance hybrid is dispersed over ~~benzene~~ benzene ring and is less available for protonation.
Aromatic amines are less basic than aliphatic amines & show no resonance.

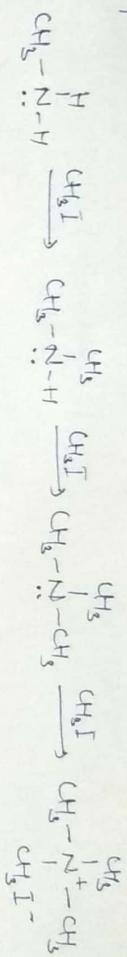
REACTIONS OF AMINES!

1) Salt formation :- Amines are basic compounds. They react with mineral acid to form salt.



TEST
4) Rea

Reaction with alkyl halide:- When treated with excess of alkyl halide, hydrogen atom attached to N are replaced successively by alkyl groups to give quaternary ammonium salt as final product.

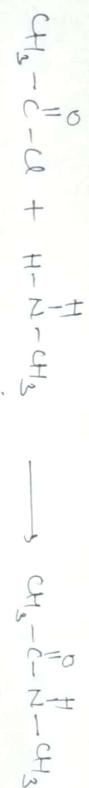


3) Reaction with Acid chlorides:- Amines react with acid chlorides

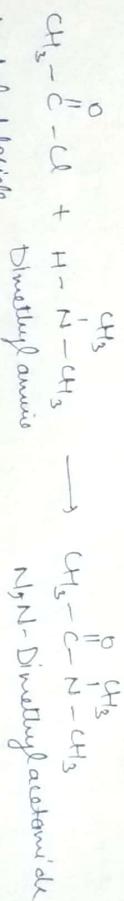
To give amides. 1° amine gives N-substituted amide

2° amine " N,N-disubstituted amide

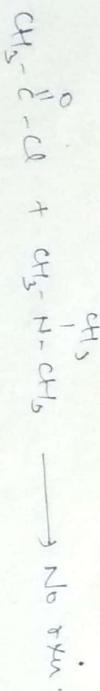
3° amine doesn't react



Acetyl chloride Methyl amine N-Methyl acetamide



Acetyl chloride Dimethyl amine N,N-Dimethylacetamide



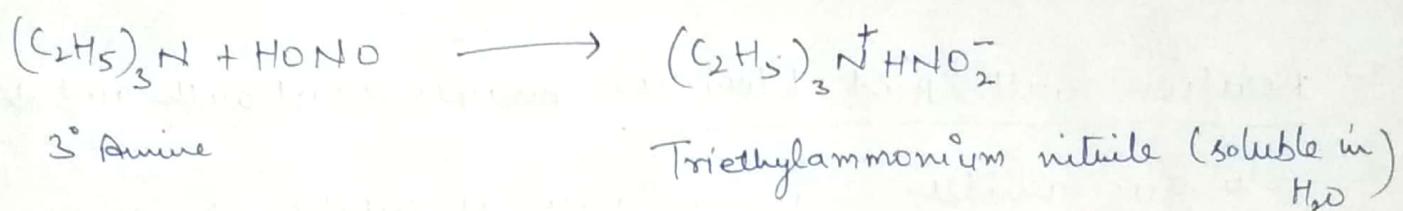
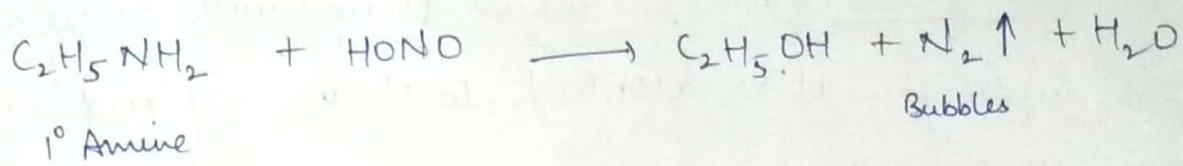
Test for Qualitative Identification of 1°, 2° & 3° Amines:

4) Reaction with nitrous acid:- On reaction with HNO_2

1° amine gives alcohol and N_2 gas

2° " " Nitrosoamine (H_2O insoluble yellow sol)

3° " " Trialkylammonium nitrate salt (H_2O soluble)



5) Carbylamine test or isocyanide test: - 1° amines react with KOH in ethanol to form isocyanide & have very offensive smell.
 2° and 3° amines doesn't give this test.

