



# STUDENT STUDY PROJECT

2018-2019



Title of the project: **Amines**

Submitted by:

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Guided by: Dr SB Ronald

# AMINES

## History of Amines :-

Industrially the synthesis of methyl amines in batch mode from methanol and ammonia, using zinc chloride, was first reported in 1884.

The first report of animation of alcohols in the gas was in 1909.

Methyl amines were first made commercially in the 1920s for use in the tanning industry for the dehairing of animal skins by commercial solvents corporation in Terra haute, Indiana.

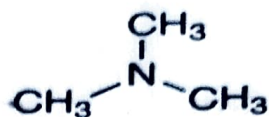
## INTRODUCTION :-

Amines are organic compounds that are derived by replacing one or more hydrogen atoms of Ammonia with hydrocarbon groups.

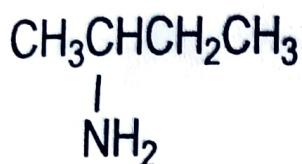
Amines are organic derivatives of Ammonia ( $\text{NH}_3$ ), in which one or more alkyl, cycloalkyl or aromatic groups replace hydrogen and bond to the nitrogen atom.



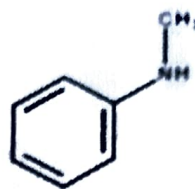
Methyl amines



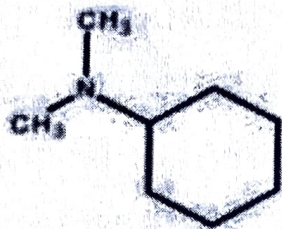
Tri methylamine.



Methyl propylamine



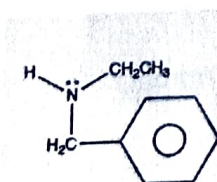
Methyl phenylamine



Cyclohexyl dimethylamine

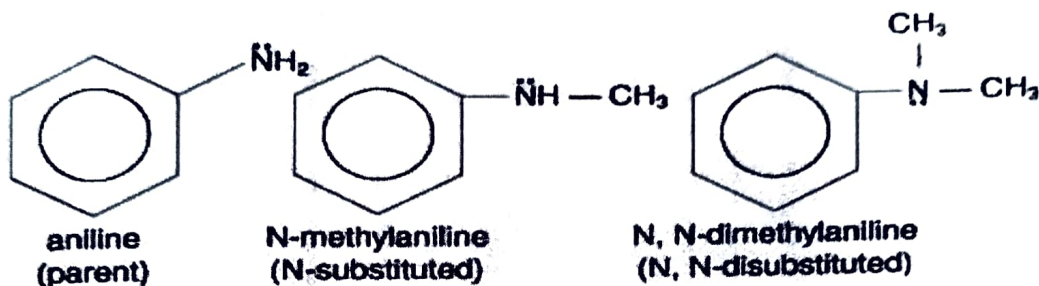
## Aliphatic amines :-

An amine in which nitrogen is bonded only to alkyl groups.



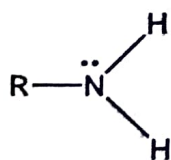
## Aromatic amines :-

An amine in which nitrogen is bonded to one or more aryl groups.

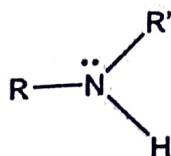


## Classification for Amines :-

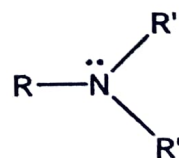
Amines are classified as primary, secondary or tertiary depending upon the degree of substitution at the nitrogen atom. An amine with one alkyl/aryl group attached to nitrogen is a primary amine. If there are two or three alkyl/aryl groups bonded to nitrogen, then the said amines are classified as secondary and tertiary respectively.



Primary



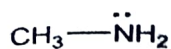
Secondary



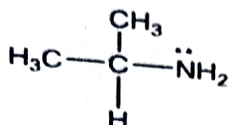
Tertiary



## Primary Amines



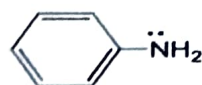
Methylamine



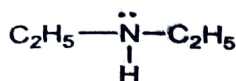
Isopropylamine



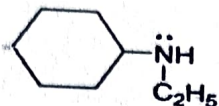
Cyclohexylamine

Phenylamine  
(aniline)

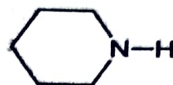
## Secondary Amines



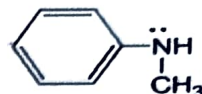
Diethylamine



N-cyclohexylethylamine

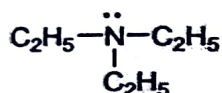


Piperidine

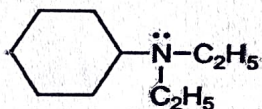


N-methylaniline

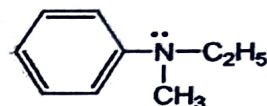
## Tertiary Amines



Triethylamine

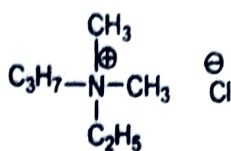
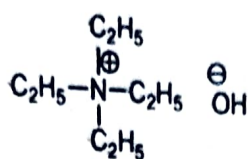
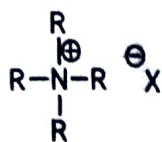


N,N-cyclohexyldiethylamine



N-ethyl-N-methylaniline

Besides, the above three amines in which the nitrogen is bonded to one, two or three alkyl/aryl substituents. There is another class of compound in which nitrogen may also be bonded to four alkyl/aryl groups. Such category of compounds are called quaternary ammonium salts. The nitrogen atom, which bears a positive charge in these compounds is named as an ammonium ion



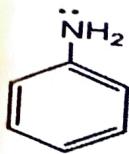
Quaternary ammonium salt    Tetraethylammonium hydroxide    Ethyldimethylpropylammonium chloride

## Nomenclature :-

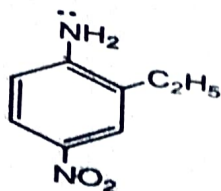
- Simple 1°, 2°, and 3° amines: common (trivial) names are obtained by alphabetically arranging the names of the alkyl substituents on the nitrogen and adding the suffix -amine (e.g., ethylmethylaniline).
- Amines in the IUPAC system: the "e" ending of the alkane name for the longest chain is replaced with -amine. The amine group is located by the position number. Groups that are attached to the nitrogen atom are located using "N" as the position number. More complex primary amines are named with —NH<sub>2</sub> as the amino substituent.
- Aromatic amines: named as derivatives of the parent compound aniline. Substituents attached to the nitrogen are indicated by using "N-" as the location number.

IUPAC nomenclature retains the common name aniline for the amino substituted derivative of benzene. Substituted derivatives of aniline are numbered beginning from carbon that bears the amino group.

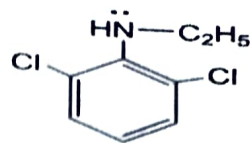




Aniline

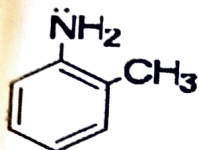


2-ethyl-4-nitroaniline

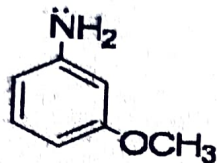


2,6-dichloro-N-ethylaniline

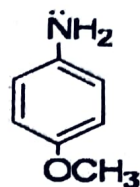
Many aromatic amines like toluidines and anisides are still known by their historical names.



o-Toluidine  
(2-Methylaniline)



m-Anisidine  
(3-Methoxyaniline)

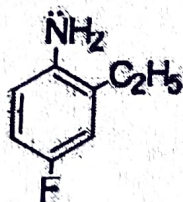


p-Anisidine  
(4-Methoxyaniline)

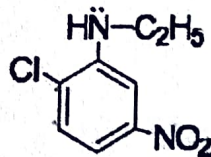
Aromatic amines have also been named as arenamines. Thus aniline the parent compound of the aromatic family is listed as benzenamine.



Aniline  
(benzenamine)

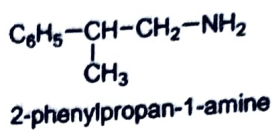
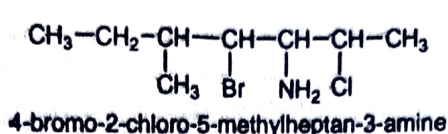
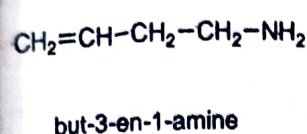
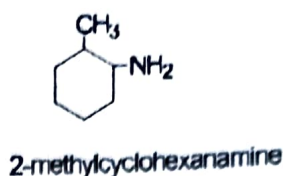
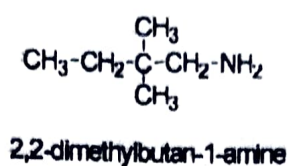
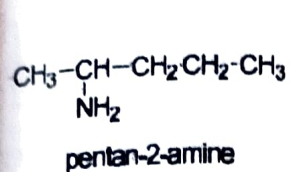


2-ethyl-4-fluoroaniline  
(2-ethyl-4-fluorobenzenamine)



2-chloro-5-nitro-N-ethylaniline  
(2-chloro-5-nitro-N-ethylbenzenamine)

**Substitutive nomenclature:** The most widely used system of substitutive amine nomenclature is the one adopted by Chemical Abstracts- a comprehensive index of chemical literature. In this system the compounds are named as follows:



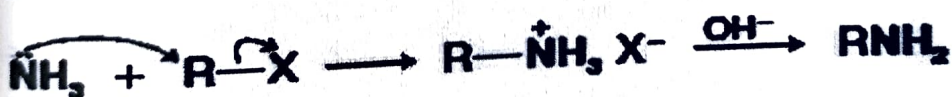
## Preparations :-

### Nucleophilic substitution Reaction :-

Alkylation of Ammonia Salts of primary amines can be prepared from ammonia and alkyl halides by nucleophilic substitution reactions.

Subsequent treatment of the resulting aminium salts with a base gives primary amines:

This method is of very limited synthetic application because multiple alkylations occur.



When ethyl bromide reacts with ammonia, for example, the ethylaminium bromide that is produced initially can react with ammonia to liberate

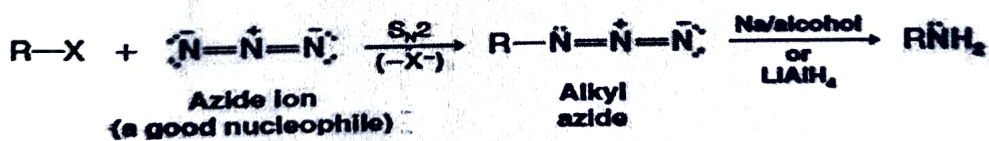


ethylamine. Ethylamine can then compete with ammonia and react with ethyl bromide to give diethylaminium bromide.

- Repetitions of alkylation and proton transfer reactions ultimately produce some tertiary amines and even some quaternary ammonium salts if the alkyl halide is present in excess.

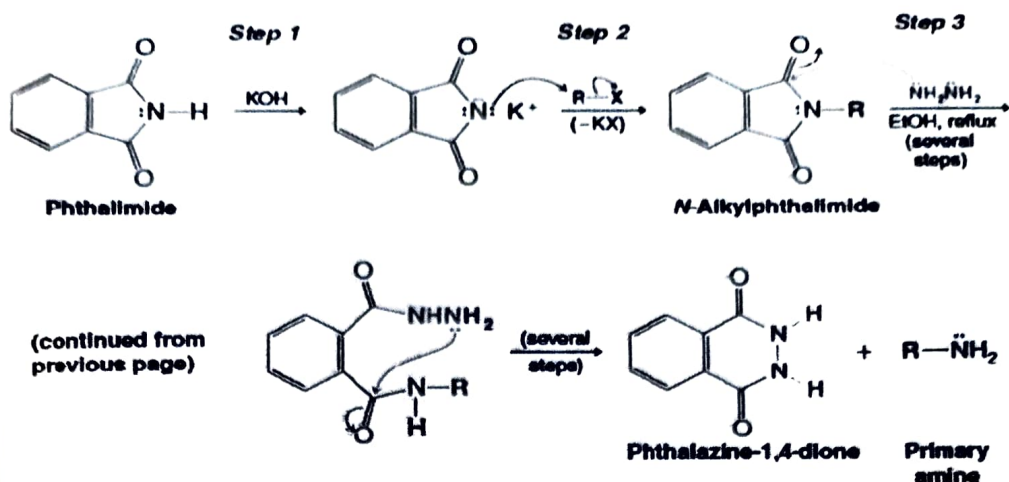
## Alkylation of Azide ion and Reduction :-

- A much better method for preparing a primary amine from an alkyl halide is first to convert the alkyl halide to an alkyl azide ( $R-N_3$ ) by a nucleophilic substitution reaction, then reduce the azide to a primary amine with sodium and alcohol or with lithium aluminum hydride.



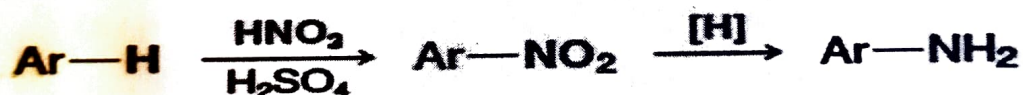
## Gabriel synthesis :-

- Potassium phthalimide (see the following reaction) can also be used to prepare primary amines by a method known as the Gabriel synthesis:



## Reduction of Nitro compounds:-

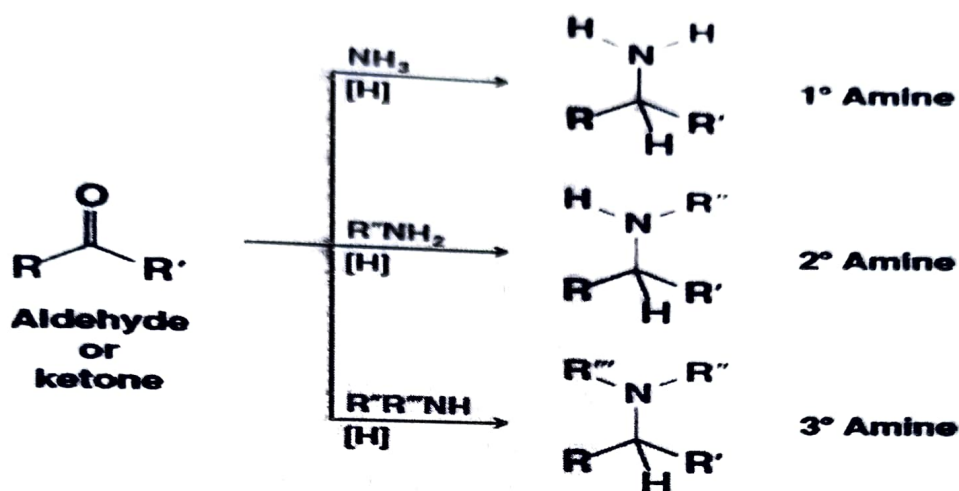
- Preparation of Aromatic Amines through Reduction of Nitro Compounds
- The most widely used method for preparing aromatic amines involves nitration of the ring and subsequent reduction of the nitro group to an amino group:



## Reductive amination :-

- Preparation of Primary, Secondary, and Tertiary Amines through Reductive Amination
- Aldehydes and ketones can be converted to amines through catalytic or

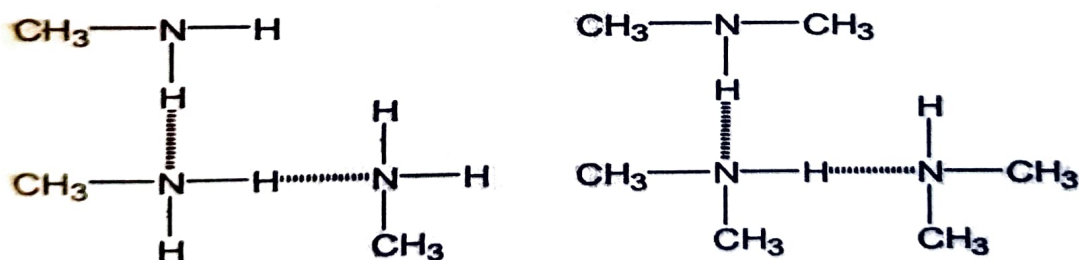
chemical reduction in the presence of ammonia or an amine. Primary, secondary, and tertiary amines can be prepared this way:



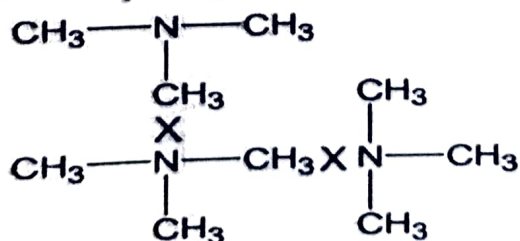
## Physical Properties :-

### 1. Hydrogen Bonding :-

1° and 2° amines can hydrogen bond to each other:



• 3° amines cannot hydrogen bond to each other:



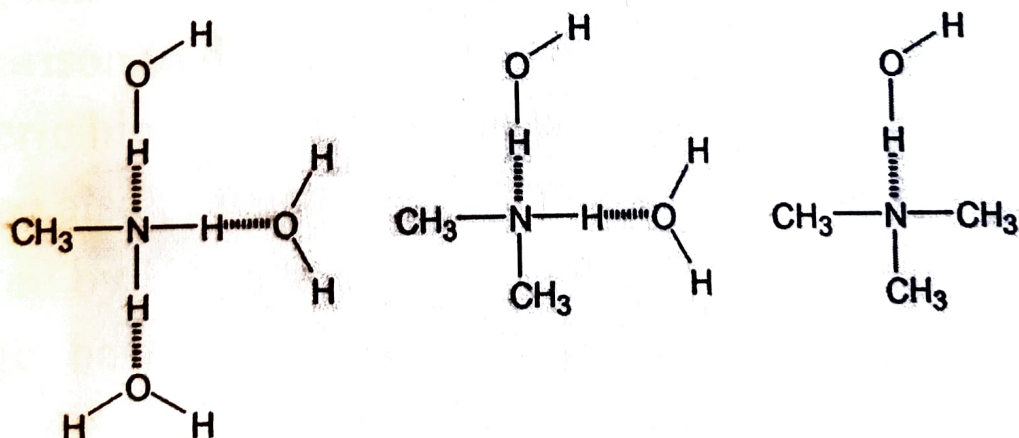


## 2. Boiling Point:-

- Nitrogen is less electronegative than oxygen, so the N—H bond is not quite as polar as the O—H bond.
- Hydrogen bonds from N—H's are not as strong as those resulting from O—H's.
- Hydrogen bonding between 1° and 2° amines is not as strong as those found in alcohols or carboxylic acids.
- 1° and 2° amines have lower boiling points than alcohols of similar molecular weight.
- 3° amines, since they do not hydrogen bond to each other, have boiling points similar to hydrocarbons of the same molecular weight.

## 3. Water solubility :-

- 1°, 2°, and 3° amines can all form hydrogen bonds with water.
- Low-molecular weight amines are generally water-soluble.



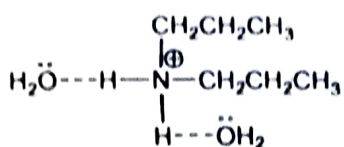
#### 4. Steric effect :-

Thus it can be said that the basicity of amine in gaseous phase depends largely on the +I effect of the alkyl group. But this basicity order of amines does not hold true in aqueous solution. In aqueous phase tertiary amines are weaker bases even in comparison to primary amines. This altered order of amine basicity in solution is due to solvation effect.

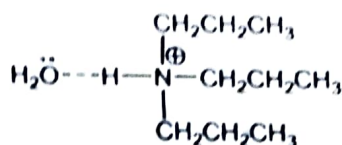
Basicity in aqueous phase:  $(\text{CH}_3\text{CH}_2)_2\text{NH} > \text{CH}_3\text{CH}_2\text{NH}_2 > (\text{CH}_3\text{CH}_2)_3\text{N} > \text{NH}_3$

Alkyl substitution increases the ability of ammonium cation to disperse its positive charge but it decreases its ability to form hydrogen bond with water molecules. In case of secondary amines the dialkylammonium cation formed still has two hydrogens to undergo hydrogen bonding, whereas in case of tertiary amines, the trialkylammonium cation has only one hydrogen available for hydrogen bonding. As a result trialkylammonium cation is less stabilized in comparison to dialkylammonium cation. Besides this, the steric hindrance of the three-alkyl groups on t-amine also prevents the lone pair of electron to be attacked by  $\text{H}^+$  ions. Hence secondary amines are stronger bases than tertiary amines.





Dipropylammonium cation  
(two hydrogen available for  
bonding)

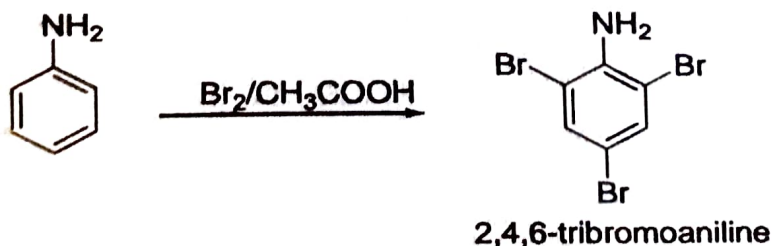


Tripropylammonium cation  
(only one hydrogen available  
for bonding)

## Substitution Reaction :-

Besides the reactions of the amino group, aryl amines also undergo electrophilic aromatic substitution reaction. Amino group activates the aromatic ring for further electrophilic substitution reaction because of the delocalization of the lone pair of electron on the nitrogen atom over to the benzene ring.

The amino group is thus activating and ortho-para directing. The group is so activating that it is difficult to prevent its polysubstitution. For example bromination of aniline instead of o- bromo aniline and p-bromo aniline yields a single 2,4,6-tribromoaniline.

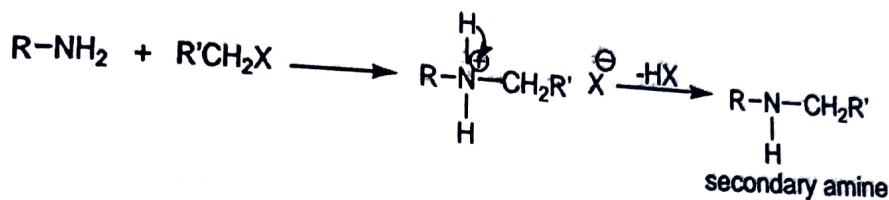




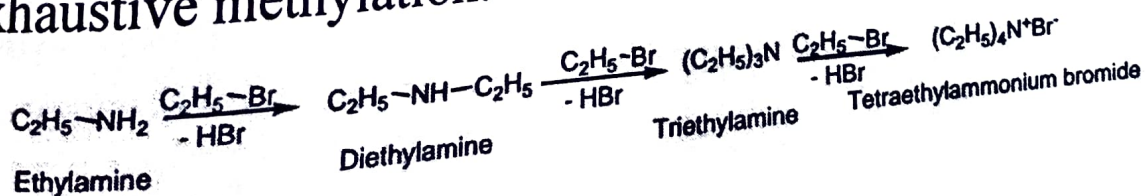
# Chemical properties :-

## 1. Alkylation :-

Reaction of an amine with alkyl halide, result in alkylation of the nitrogen. The reaction takes place by  $S_N2$  mechanism with the amine acting as a nucleophile.



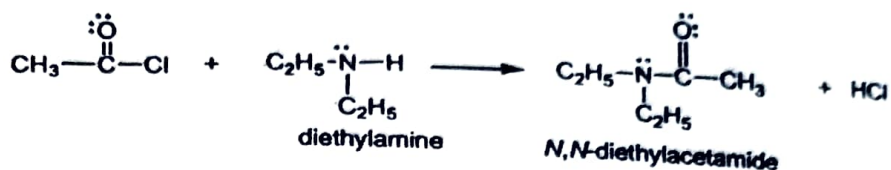
The initial product of the reaction is infact an alkylammonium ion and if N-H bond is still available then further alkylation may take place. It is for this reason that primary amine on reaction with alkyl halide yields secondary amine. Secondary amine on alkylation yields tertiary amine. The reaction may not stop at this stage and tertiary amine may itself be alkylated, yielding quaternary ammonium salts. Hence this procedure is also known as exhaustive alkylation. However if the alkyl halide used is methyl iodide, then the process is commonly referred to exhaustive methylation.



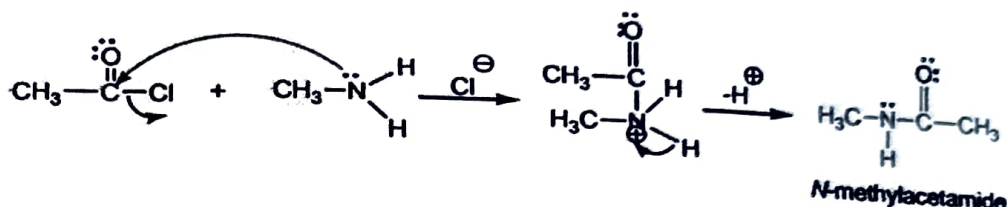
Since a mixture of product results, thus alkylation of amines is not a good method for introducing alkyl group into an amine.

## 2. Acylation :-

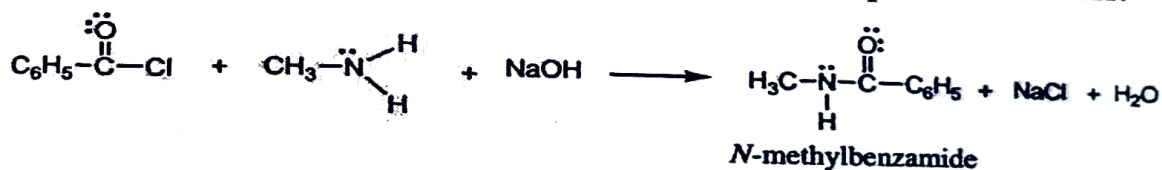
Primary and secondary amines undergo nucleophilic acyl substitution reaction when treated with acyl halides or anhydrides forming N-substituted amides.



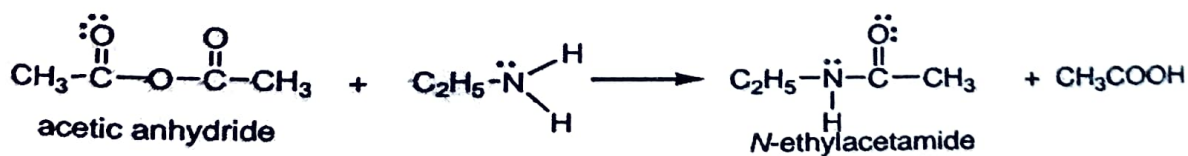
Mechanism:



Benzoylation of amines is carried out by treating amine with benzoyl chloride in presence of aqueous alkali.



Acylation of amines to substituted amides is also achieved by treating them with carboxylic anhydrides.



### 3. Carbylamine reaction :-

Primary amines react with chloroform in presence of alkali to form isonitrile or carbylamines, which have extremely unpleasant nauseating odour. This reaction is therefore used as a qualitative diagnostic for primary amines.



Mechanism:

