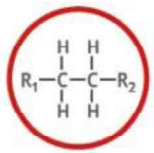
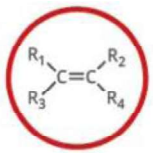
FUNCTIONAL GROUPS IN ORGANIC CHEMISTRY

FUNCTIONAL GROUPS ARE GROUPS OF ATOMS IN ORGANIC MOLECULES THAT ARE RESPONSIBLE FOR THE CHARACTERISTIC CHEMICAL REACTIONS OF THOSE MOLECULES. IN THE GENERAL FORMULAE SHOWN BELOW FOR EACH FUNCTIONAL GROUP, 'R' REPRESENTS THE REST OF THE MOLECULE, AND 'X' REPRESENTS ANY HALOGEN ATOM.

HYDROCARBONS | SIMPLE OXYGEN HETEROATOMICS | HALOGEN HETEROATOMICS | CARBONYL COMPOUNDS | NITROGEN-BASED | SULFUR-BASED | AROMATIC

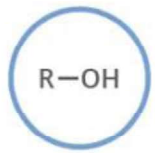


ALKANE
Naming: -ane
e.g. ethane

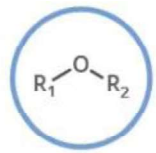


ALKENE
Naming: -ene
e.g. ethene

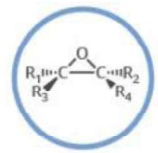
ALKYNE
Naming: -yne
e.g. ethyne



ALCOHOL
Naming: -ol
e.g. ethanol



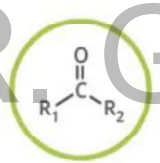
ETHER
Naming: -oxy -ane
e.g. methoxyethane



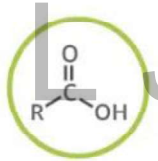
EPOXIDE
Naming: -ene oxide
e.g. ethene oxide

HALOALKANE
Naming: halo-
e.g. chloroethane

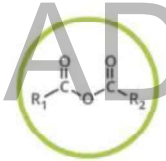
ALDEHYDE
Naming: -al
e.g. ethanal



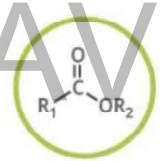
KETONE
Naming: -one
e.g. propanone



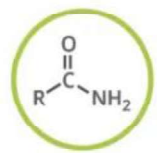
CARBOXYLIC ACID
Naming: -oic acid
e.g. ethanoic acid



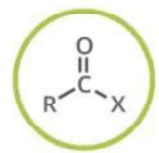
ACID ANHYDRIDE
Naming: -oic anhydride
e.g. ethanoic anhydride



ESTER
Naming: -yl -oate
e.g. ethyl ethanoate



AMIDE
Naming: -amide
e.g. ethanamide



ACYL HALIDE
Naming: -oyl halide
e.g. ethanoyl chloride

AMINE
Naming: -amine
e.g. ethanamine

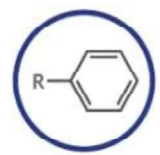
NITRILE
Naming: -nitrile
e.g. ethanenitrile

IMINE
Naming: -imine
e.g. ethanimine

ISOCYANATE
Naming: -yl isocyanate
e.g. ethyl isocyanate

AZO COMPOUND
Naming: azo-
e.g. azoethane

THIOL
Naming: -thiol
e.g. methanethiol

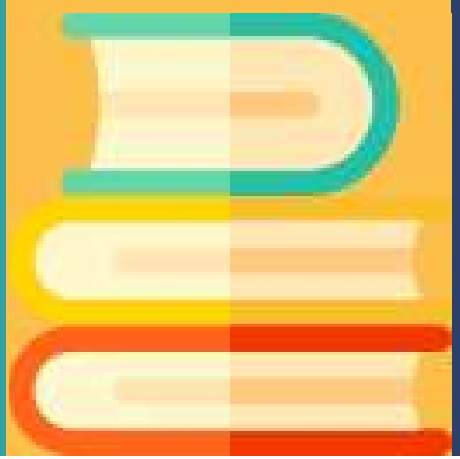


ARENE
Naming: -yl benzene
e.g. ethyl benzene

Nitrogen Containing
Functional Group

Amines

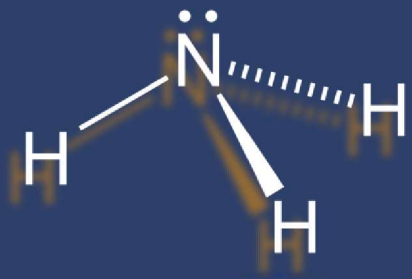
Syllabus



Organic Compounds of Nitrogen: Amines: Classification of amines (Aliphatic and Aromatic) Basicity of amines,
effect of substituent on basicity of amines
Preparation of amines
Reactions of primary alkyl & aryl amines
Chemical reactions of Aniline: Electrophilic substitution
Diazotization of Aniline and reactions of Diazonium salt
Hinsberg Reaction
Preparation and important reactions of nitro compounds, nitriles and isonitriles

Introduction

Replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl group



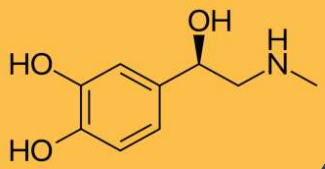
Nature

proteins, vitamins, alkaloids and hormones

Synthetic

polymers, dyestuffs and drugs

Introduction



Two biologically active compounds, namely adrenaline (a hormone) and ephedrine (a drug), both containing secondary amino group, are used to increase blood pressure.

Novocain, a synthetic amino compound, is used as an anaesthetic in dentistry.

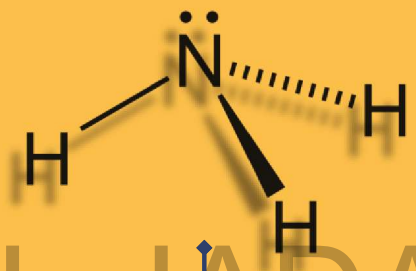
Benadryl, a well-known antihistaminic drug also contains tertiary amino group

Quaternary ammonium salts are used as surfactants

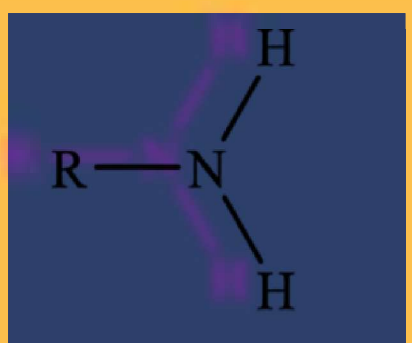
Diazonium salts are intermediates in the preparation of a `variety of aromatic compounds including dyes

Classification

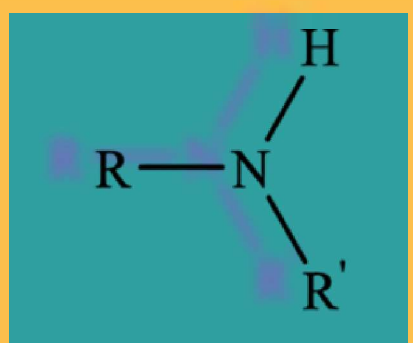
AMMONIA



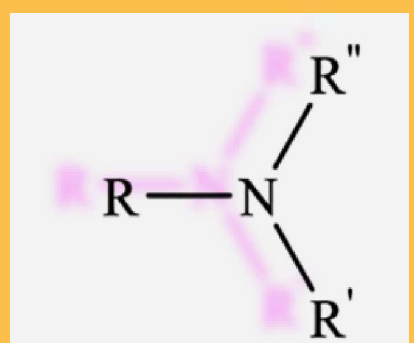
PRIMARY



SECONDARY



TERTIARY



Classification

$[NH_4]^+X^-$

Ammonium halide

$[NR_4]^+X^-$

tetra alkyl ammonium halide

$[(C_2H_5)_4N^+]Cl^-$

Tetraethyl ammonium chloride

$[(C_6H_5)_4N^+]I^-$

Tetraphenyl ammonium iodide

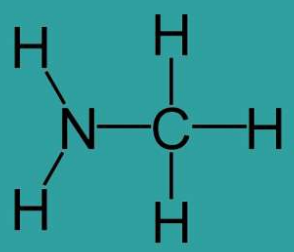
$[(CH_3)_4N^+]Br^-$

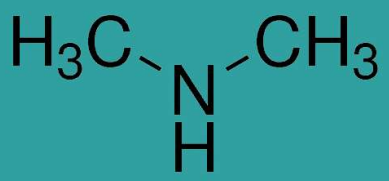
Tetramethyl ammonium bromide

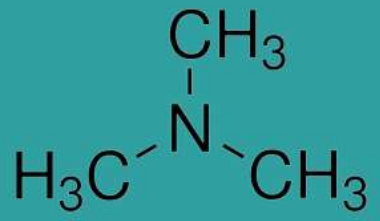
Aliphatic amines

Aromatic amines

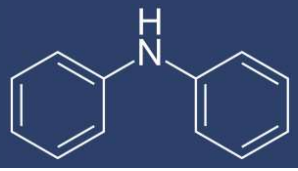
nitrogen atom may be bonded to one or more alkyl chains



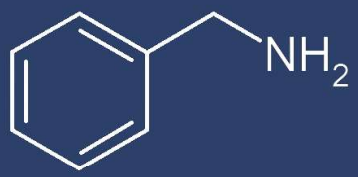


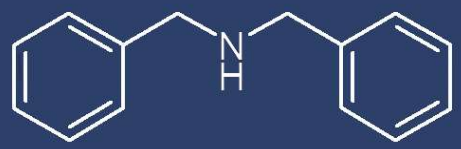


Aryl Amines



Aralkyl Amines

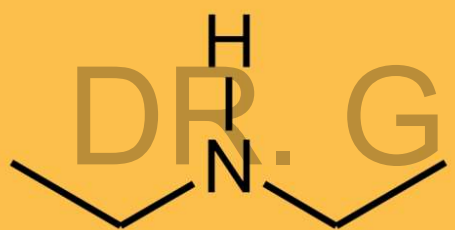


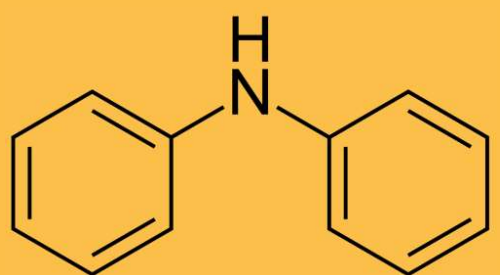


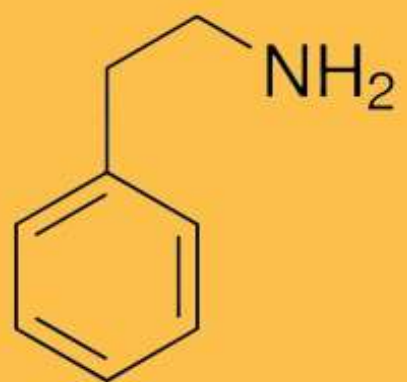
Classification

Simple and mixed Amines

Secondary and
tertiary amines





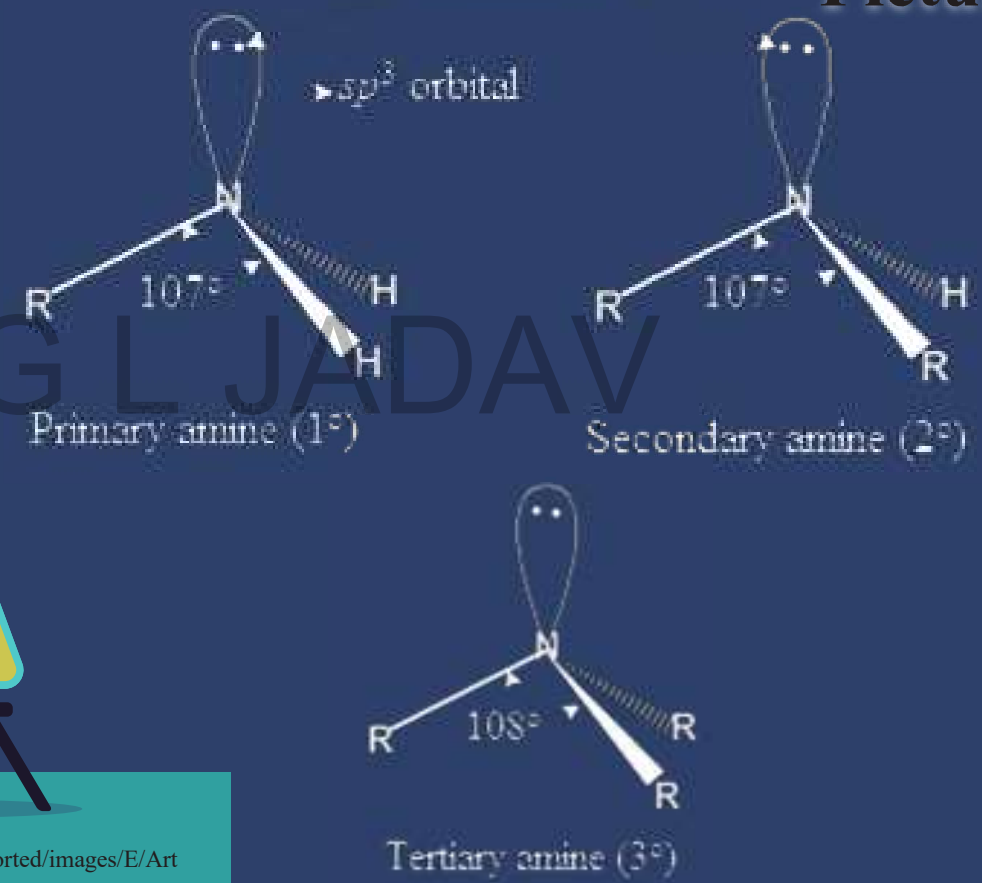


STRUCTURE

Electronic structure

STRUCTURE

Orbital Picture



P.C:-
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Preparation of

Amines

- Ammonolysis of alkyl halide
- Reduction of nitro compounds
- Reduction of amide
- Hoffmann's degradation method

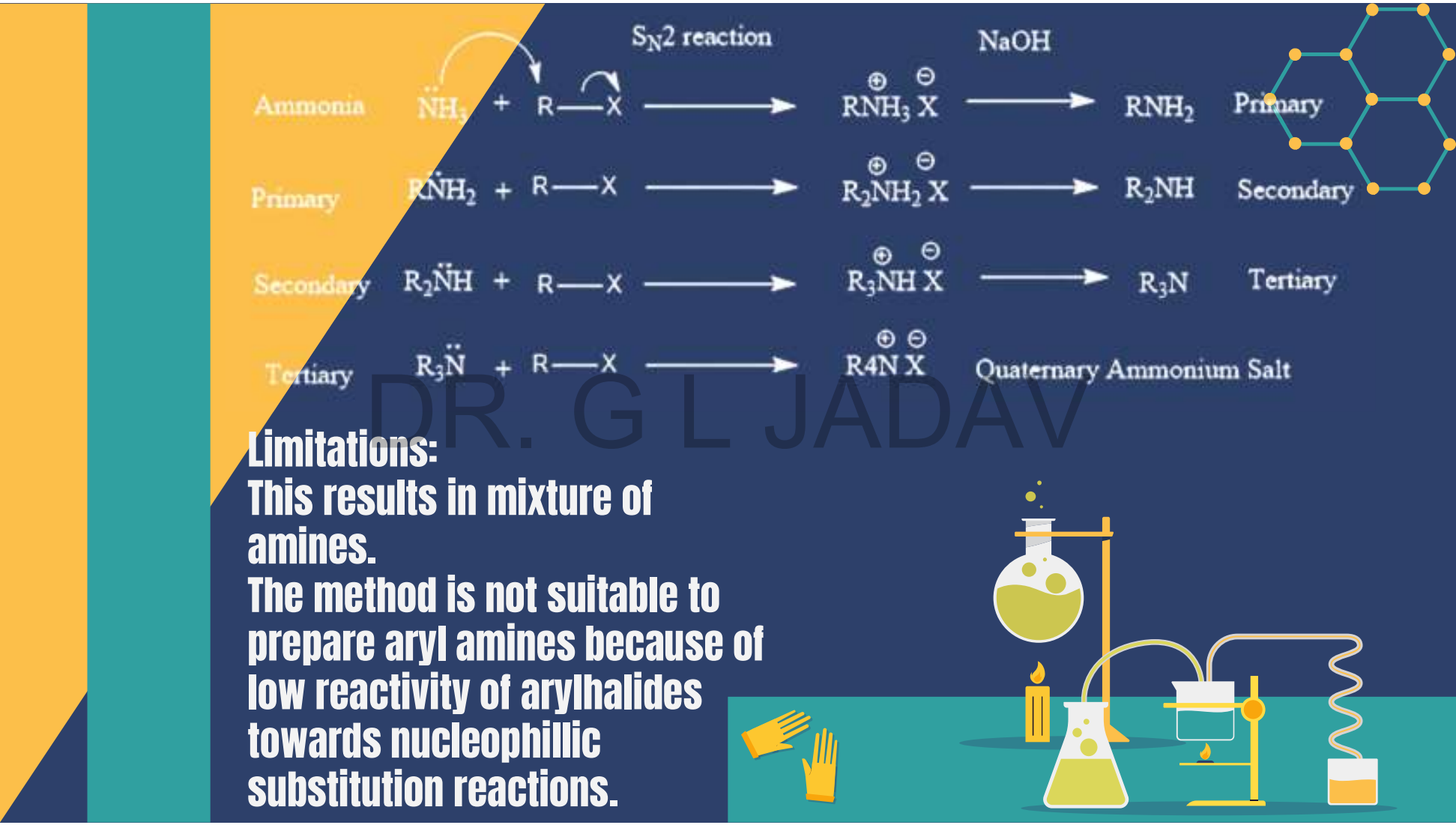
Ammonolysis of alkyl halide

Preparation of amines from alkyl halides

reduction in presence of ethanolic ammonia under a sealed tube at 373 K

cleavage of C-X bond
Replaced by -NH2

Ammonolysis
typical example of Nucleophillic Substitution reaction



Limitations:

This results in mixture of amines.

The method is not suitable to prepare aryl amines because of low reactivity of arylhalides towards nucleophillic substitution reactions.

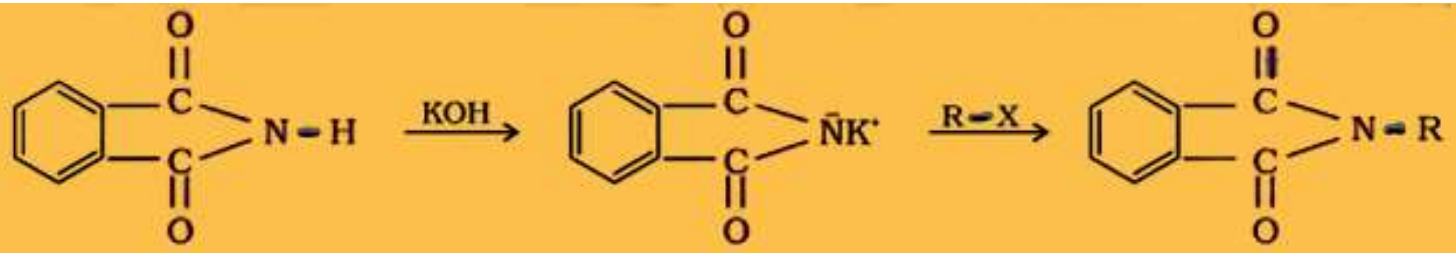
From nitro compounds

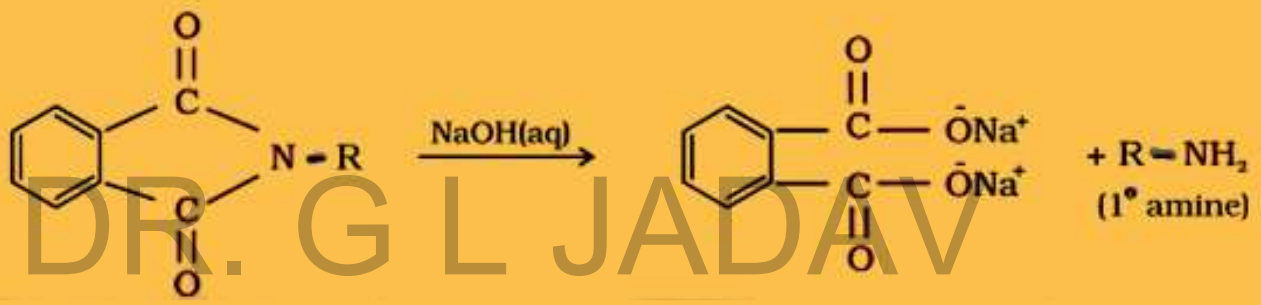
Reduction

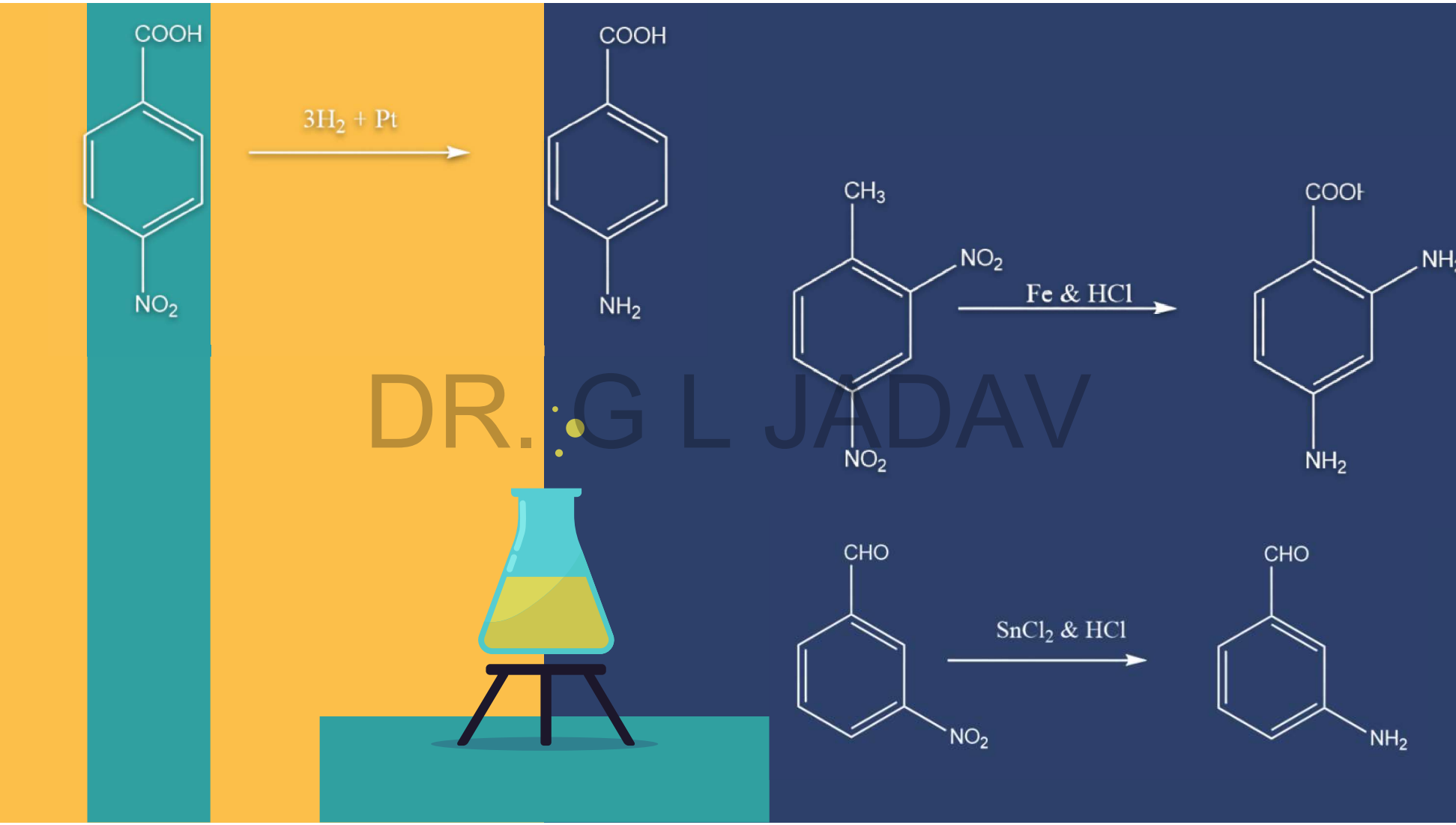
catalytic hydrogenation or by chemical means

catalytic hydrogenation reduction proceeds in presence of H2/Pt or H2/Pd whereas by chemical means using Fe/HCl or Sn/HCl

Reduction of Amide






COOH
NO2
3H2 + Pt
COOH
NH2
CH3
NO2
NO2
Fe & HCl
COOH
NH2
CHO
NO2
SnCl2 & HCl
CHO
NH2

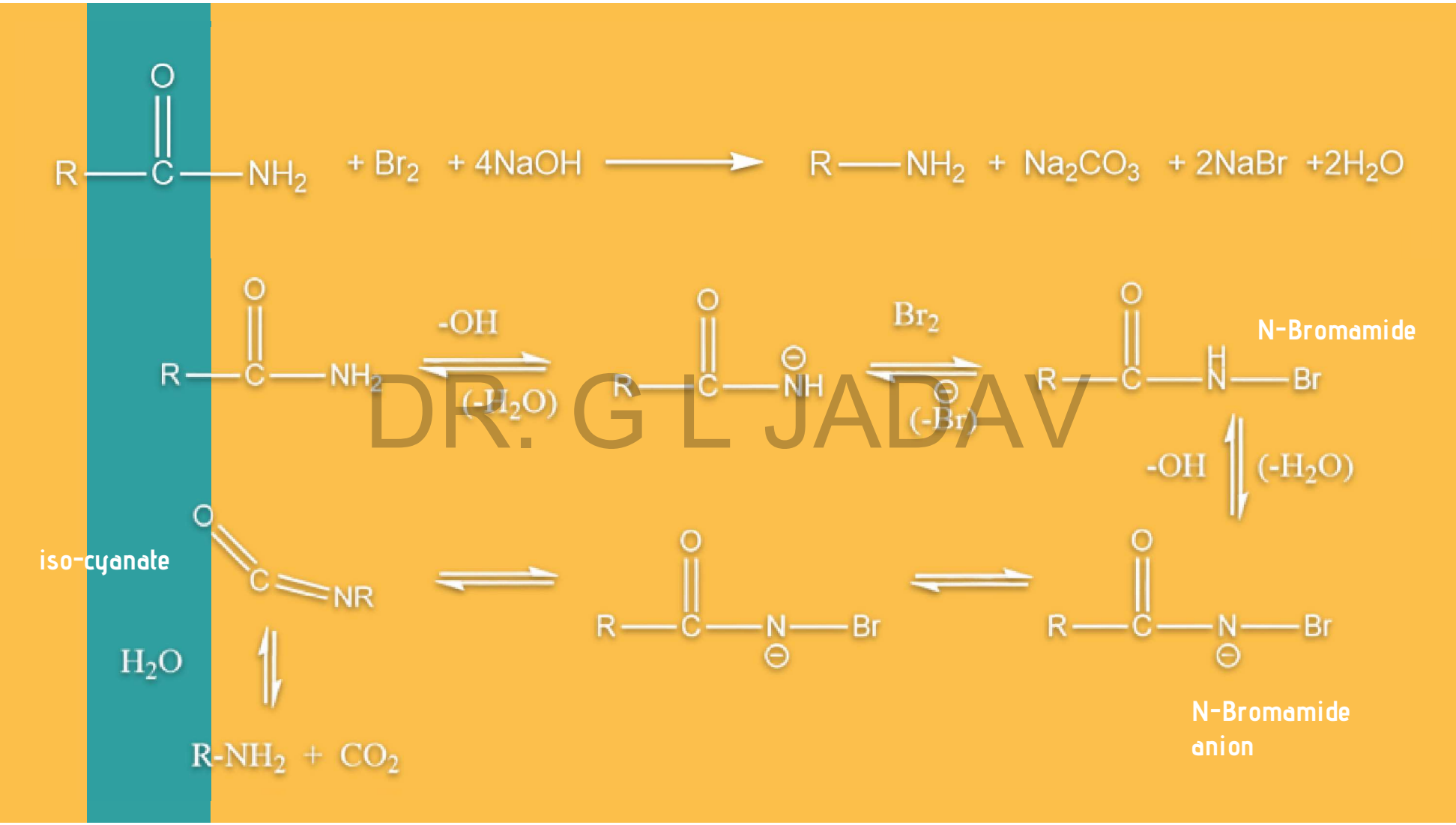
Hoffmann's Degradation of amines

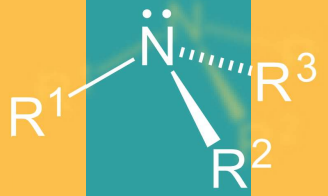
Amide with bromine in an aqueous or ethanolic solution of sodium hydroxide.

migration of an alkyl or aryl group from carbonyl carbon of the amide to the nitrogen atom

one carbon less than that present in the amide.

Hoffmann's Degradation is also known as Hoffmann's Bromamide reaction.


+ Br2 + 4NaOH
+ Na2CO3 + 2NaBr +2H2O
-OH
(-H2O)
Br2
(-Br)
N-Bromamide
-OH
(-H2O)
iso-cyanate
H2O
R-NH2 + CO2
N-Bromamide anion



Physical properties of Amines

PHYSICAL STATE SMELL

lower aliphatic amines are gaseous, higher are liquids

Lower Aromatic amines are liquids and higher are solides

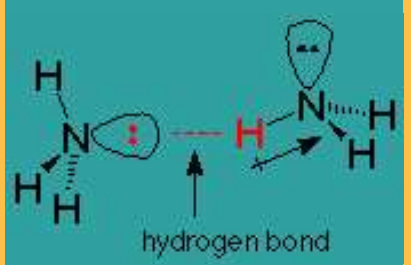
Lower amines - Ammonia smell , Higher amines-Fishey smell

Purest amines are colourless, But aerial oxidation produces colour

BOILING POINT

Primary > Secondary > Tertiary

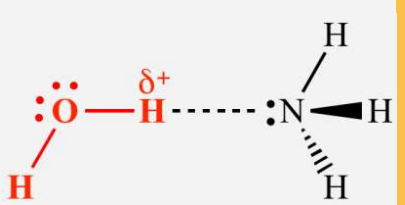
intermolecular hydrogen bonding



SOLUBILITY

Lower amines are soluble in water, Hydrogen bonding WITH WATER

Higher are insoluble (NONPOLARITY)



Name of amine	pK_b
Methanamine	3.38
N-Methylmethanamine	3.27
N,*N*-Dimethylmethanamine	4.22
Ethanamine	3.29
N-Ethylethanamine	3.00
N,*N*-Diethylethanamine	3.25
Benzenamine	9.38
Phenylmethanamine	4.70
N-Methylaniline	9.30
N,*N*-Dimethylaniline	8.92

Basic Characteristics of amines

Amines are basic in nature

Reacts with acid to forms salts

Amines have an unshared pair of electrons on nitrogen atom due to which they behave as Lewis base. Basic character of amines can be better understood in terms of their Kb and pKb values as explained below

Larger the value of Kb or smaller the value of Pkb, stronger is the base

$$K = \frac{[R\text{-}NH_3^+][OH^-]}{[R\text{-}NH2][H2O]}$$

OR

$$K[H2O] = \frac{[R\text{-}NH_3^+][OH^-]}{[R\text{-}NH_2]}$$

OR

$$K_b = \frac{[R\text{-}NH_3^+][OH^-]}{[R\text{-}NH_2]}$$

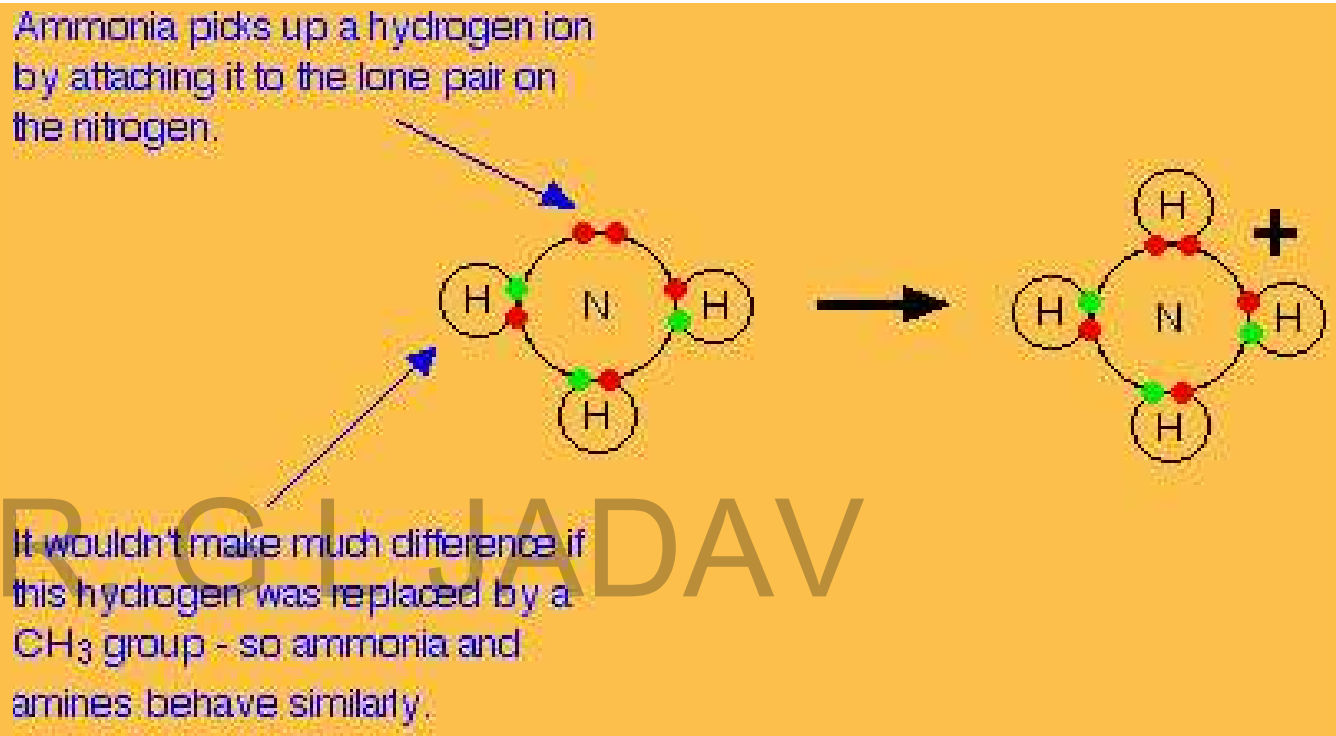
$$pk_b = -\log log\ k_b$$

Structure and basicity relationship

Basic character of an amine depends upon the ease of formation of the cation by accepting a proton from the acid. The more stable the cation is relative to the amine, more basic is the amine.

Amines are more basic than alcohols, ethers, esters etc because the N of amines is less electronegative than O, thus N can accommodate a positive charge better than O.

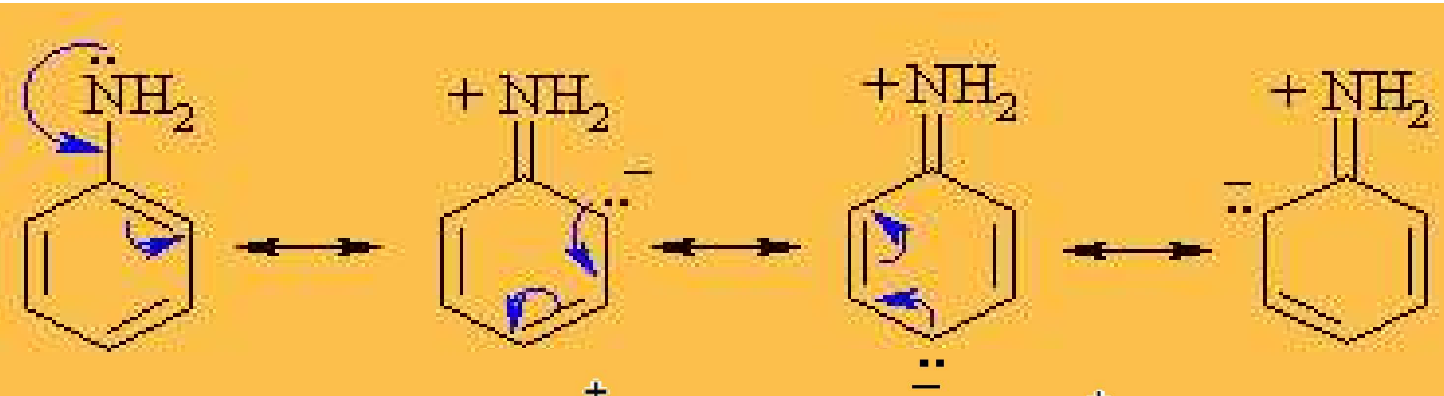
Alkanamines versus ammonia



Inductive effect of alkane

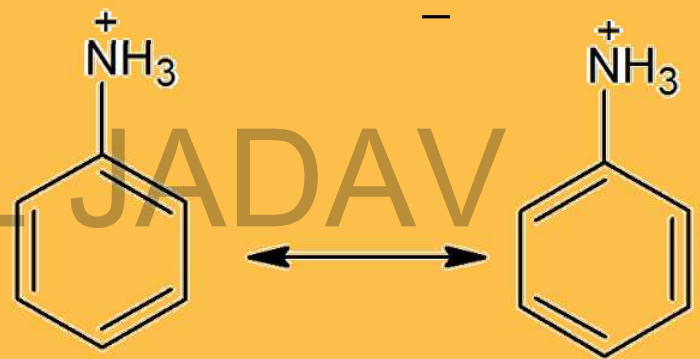
electron releasing nature of alkyl group, it pushes electrons towards nitrogen and thus makes the unshared electron pair more available for sharing with the proton of the acid. Moreover, the substituted ammonium ion formed from the amine gets stabilized due to dispersal of the positive charge by the +I effect of the alkyl group. Hence, alkylamines are stronger bases than ammonia.

Alkanamines versus ammonia



electron releasing groups like $-OCH_3$, $-CH_3$ increase basic strength

electron withdrawing groups like $-NO_2$, $-SO_3$, $-COOH$, $-X$ decrease it.



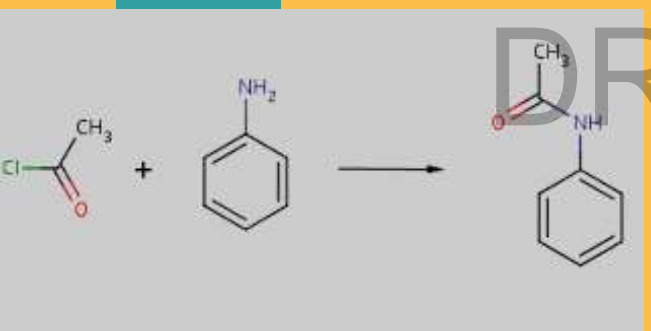
unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation. If you write different resonating structures of aniline, you will find that aniline is a resonance hybrid of the following five structures

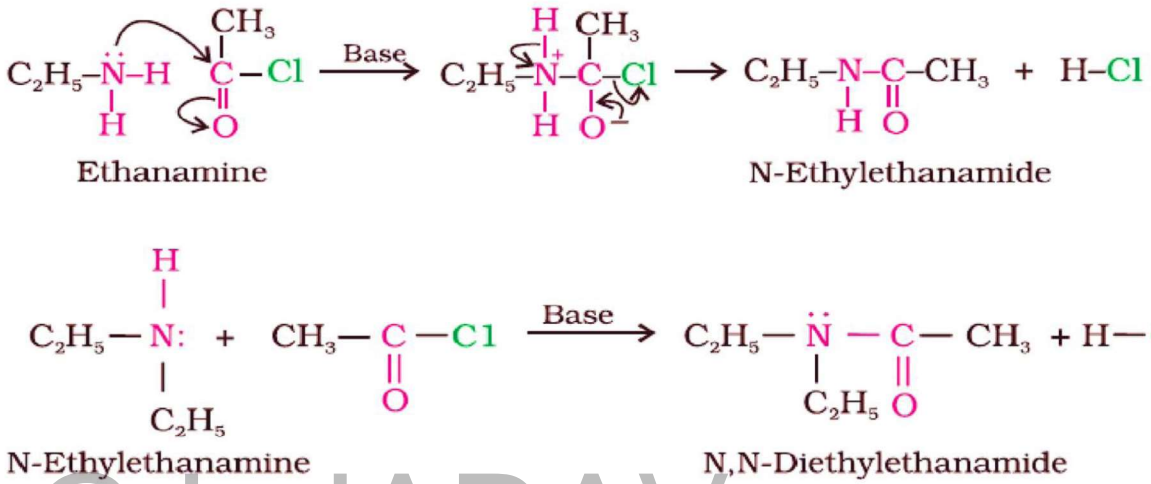
Chemical Properties of Amines

Like ammonia the primary, secondary and tertiary amines have lone pair of electrons on N atom. Thus the chemical behaviour of amine is same as that of ammonia. Amines are therefore basic in nature and thus act as a nucleophile.

1. **Reaction of amines with acid chlorides**
2. **Reaction with Alkyl halide (alkylation)**
3. **Reaction of amine with aryl sulfonyl chlorides**

Reaction of amines with acid chlorides





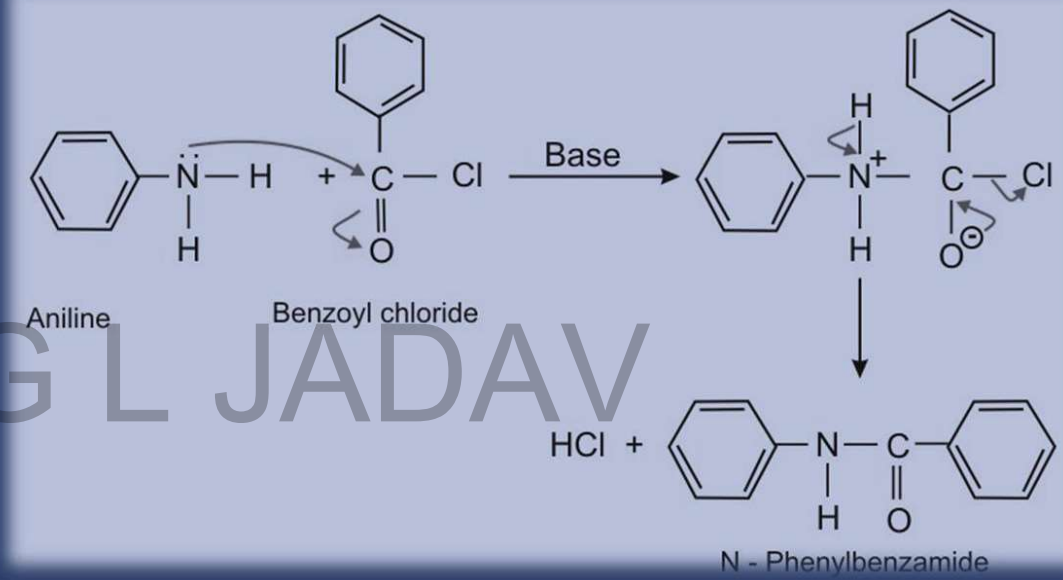
Acylation

Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophilic substitution reaction. This reaction is known as acylation. You can consider this reaction as the replacement of hydrogen atom of –NH2 or >N–H group by the acyl group. The products obtained by acylation reaction are known as amides.

aromatic amine (aniline) reacts with acid chloride to produce N-phenylethanamide or Acetanilide

$$CH_3NH_2 + C_6H_5COCl \rightarrow CH_3NHCOC_6H_5 + HCl$$

Methanamine | Benzoyl chloride | N – Methylbenzamide

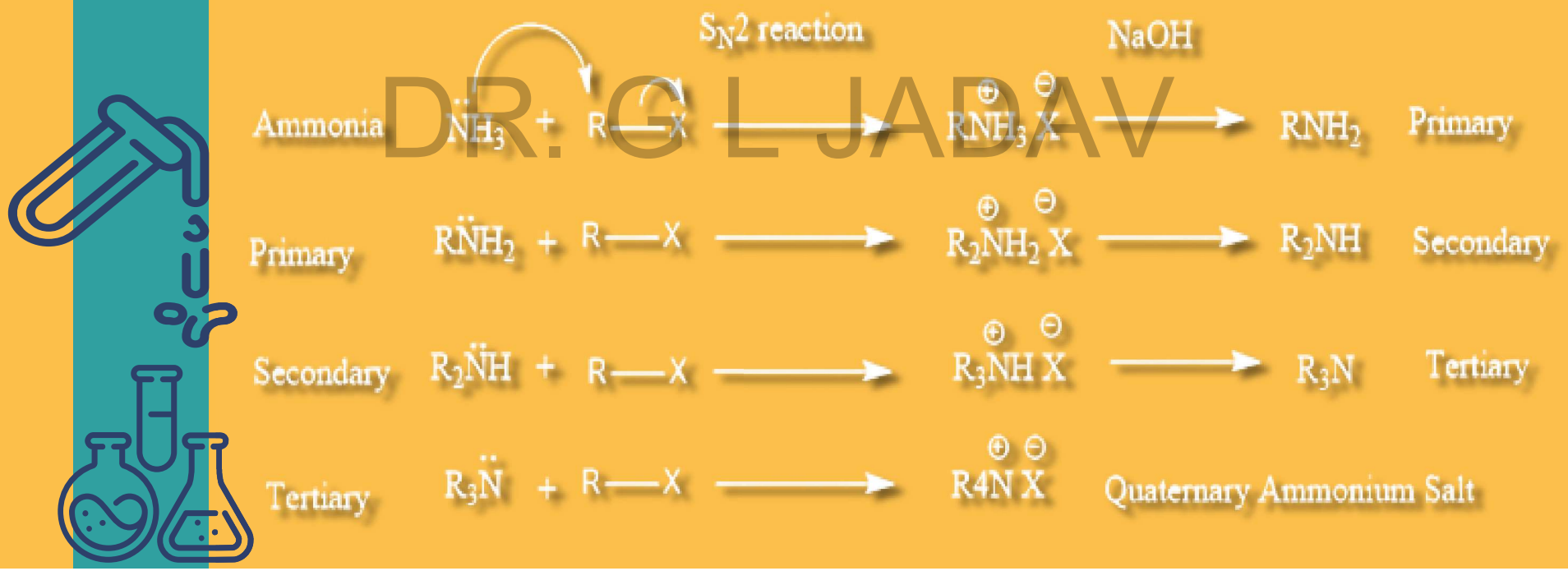


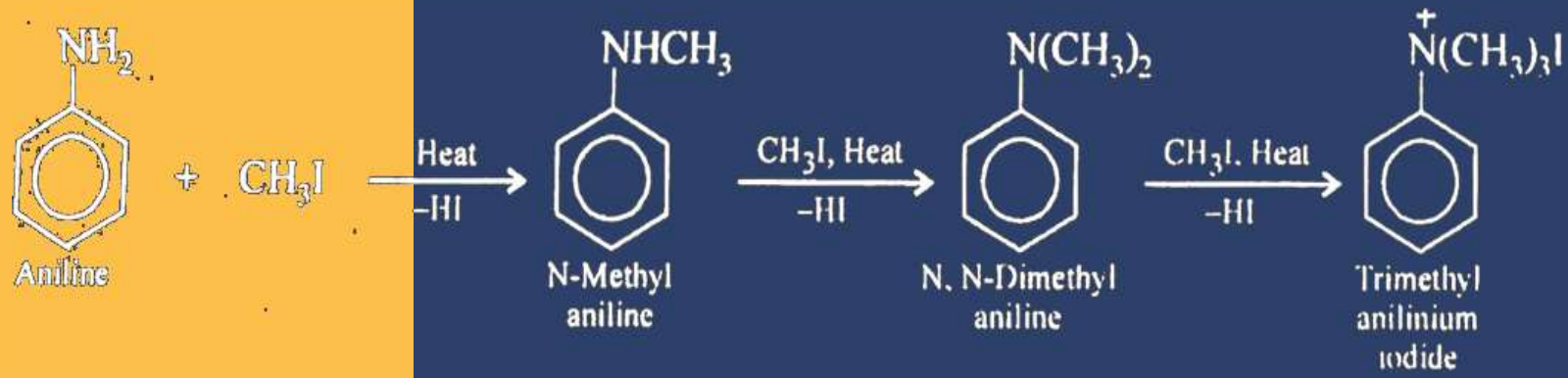
Benzoylation

Replacement of H atom by benzoyl group (C6H5-CO-) is called benzoylation. Here primary and secondary amines react with benzoyl chloride (C6H5-CO-Cl) in presence of base like pyridine/aqueous NaOH to form benzoyl derivative

Reaction with Alkyl halide (alkylation)

Amines react with alkyl halides to form amines of higher class. In this reaction the amines acts as nuclophile bringing about nucleophilic substitution reaction of alkyl halide



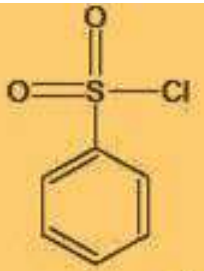


Aromatic amines also undergo similar reaction. Aniline when treated with excess of methyl iodide under high pressure results in a mixture of secondary, tertiary and quaternary salts. This reaction is also known as exhaustic methylation

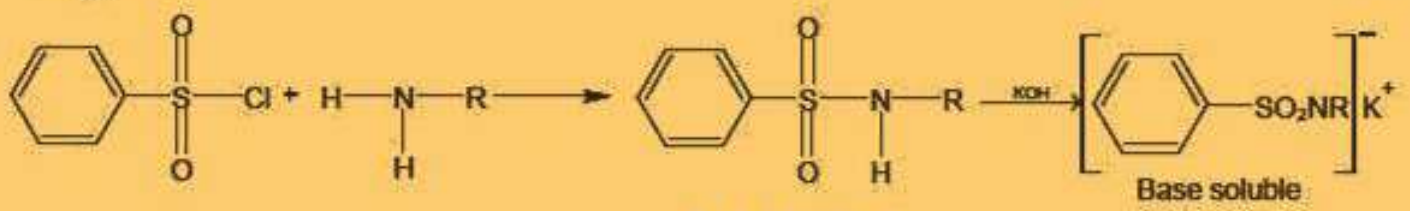
Reaction of amine with aryl sulphonyl chlorides

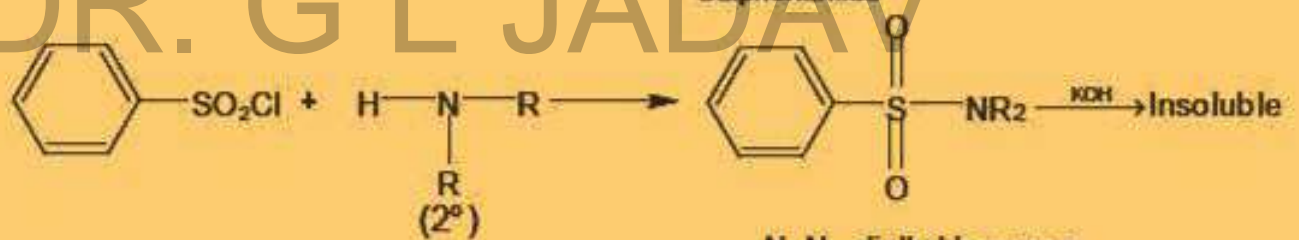
The amino group not surprisingly react with sulfonic acids similar to acid chlorides. The 1° and 2° amines reacts with benzene sulphonyl chloride ($C_6H_5SO_2Cl$) called as Hinsberg's reagent. 3° amines cannot react with this reagent because there is no hydrogen atom present in 3° amines.

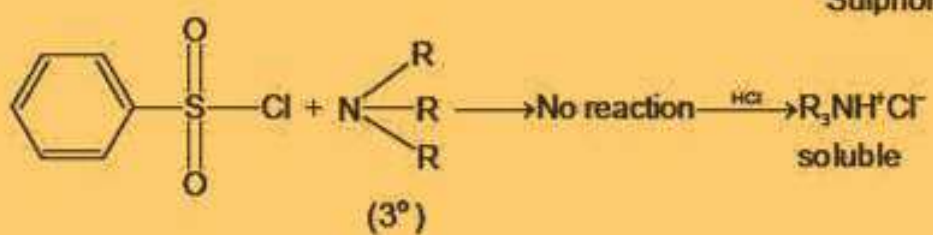
1. Primary amines :- 1° amines on reaction with Hinsberg's reagent forms N-alkyl benzene sulphonamide.
2. Secondary amines:- 2° amines on reaction with Hinsberg's reagent form N,N-dialkylbenzene sulphonamide.
3. Tertiary amines:- Do not react with Hinsberg's reagent at all.



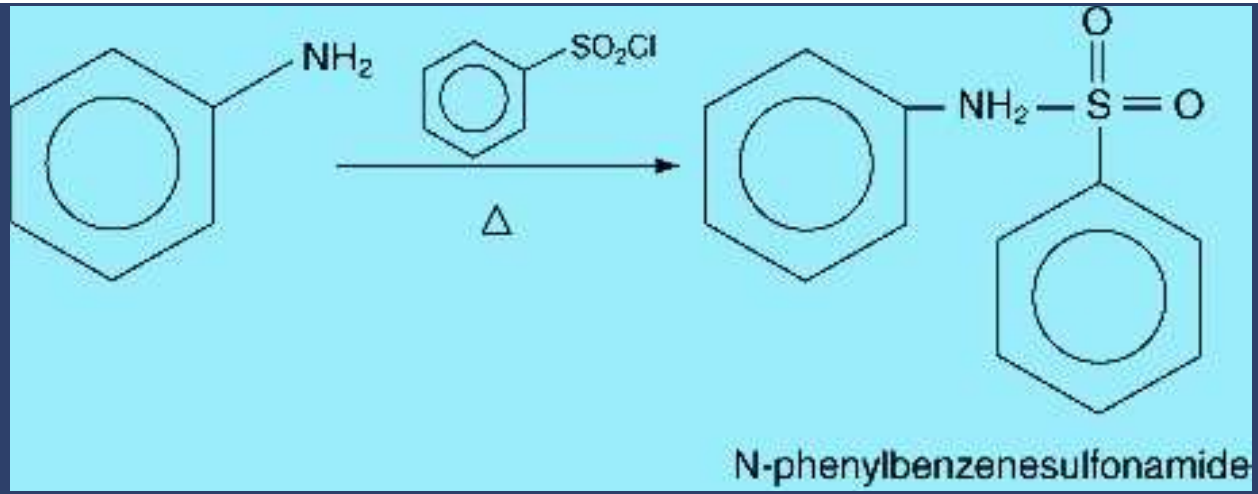
Uses:- This reaction is used to distinguish 1°, 2°, and 3° amines under the name of Hinsberg's test.







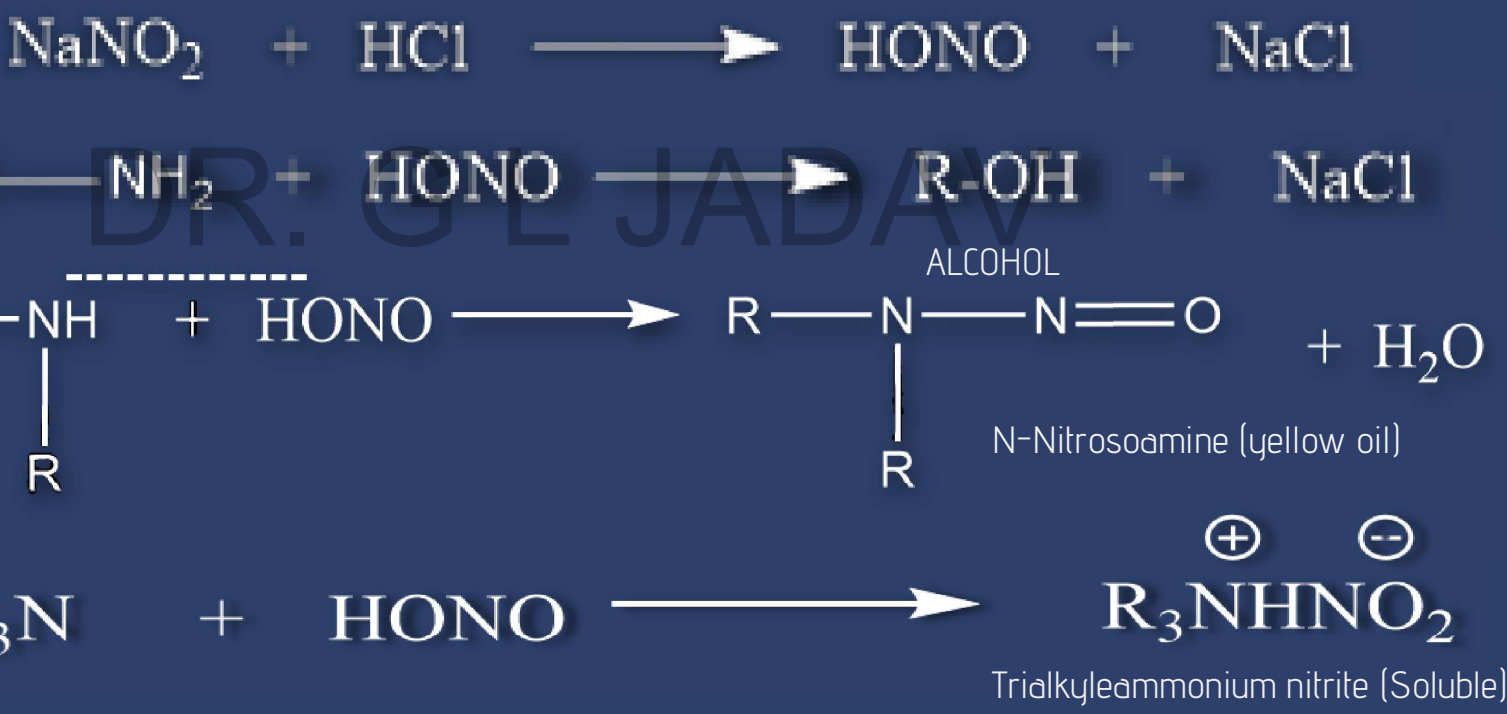
Reaction of aniline with aryl sulfonyl chloride



Substituted amides of aromatic sulfonic acids can be prepared by using the Schotten-Baumann technique. The acid chloride is added to the amine in presence of a base, either aqueous NaOH or pyridin

Reaction with Nitrous Acid (HNO_2)

Nitrous acid is unstable substance and is therefore prepared in situ by the reaction of sodium nitrite with dilute HCl at 0° C



Nitrous acid test Summary

To distinguish between primary, secondary and tertiary amines.

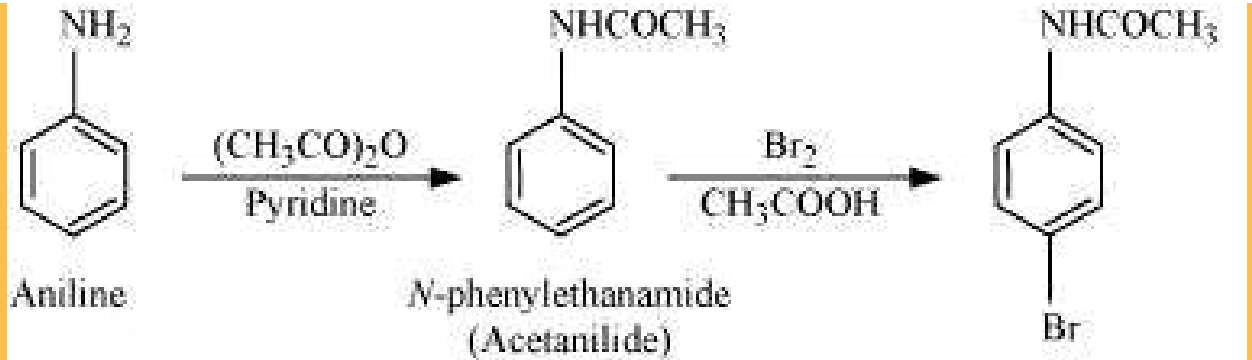
A. Primary amines react with nitrous acid to produce nitrogen gas (Seen as bubbles)
B. Secondary amines react with nitrous acid to produce yellow oily layer.
C. Tertiary amines react with nitrous acid to form soluble nitrite salts, There is no visible sign of reaction

Reactions of Aniline

Bromination of aniline

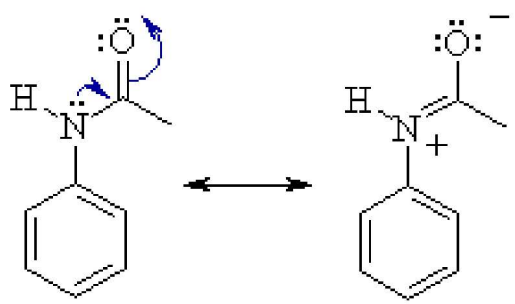
The aromatic ring in aniline is highly active due to the displacement of electron of Nitrogen towards the ring system. This results in increase in electron density on the aromatic ring. Therefore, facilitating electrophilic attack on the ring system. The substitution occurs more in ortho and para position due to the higher electron densities in these positions (resonation of aniline)

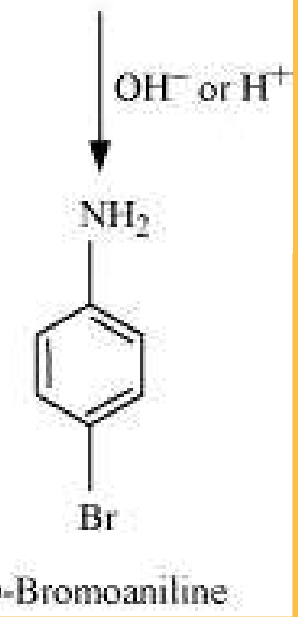
To get a mono bromo compound acetylation of aniline is carried out before bromination which on acid hydrolysis produces a monobromo aniline.



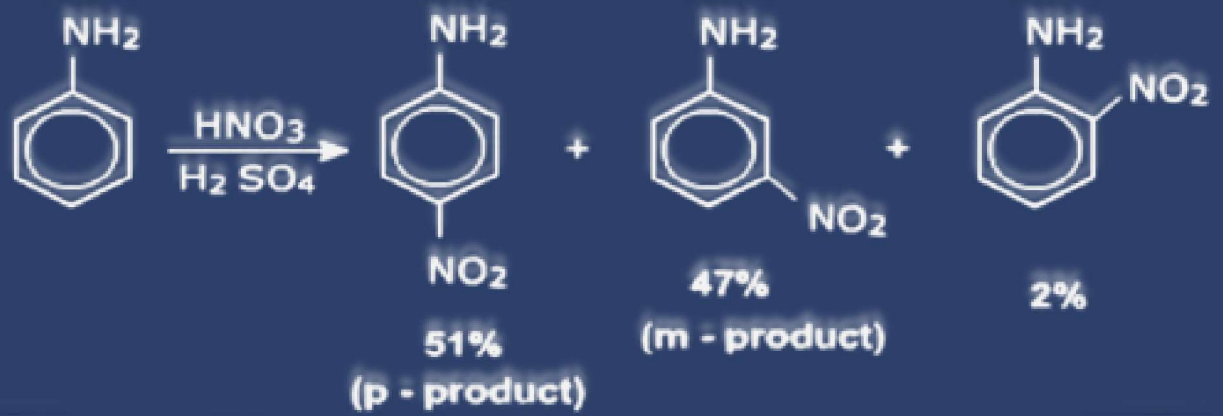
Purpose of acetylation:-

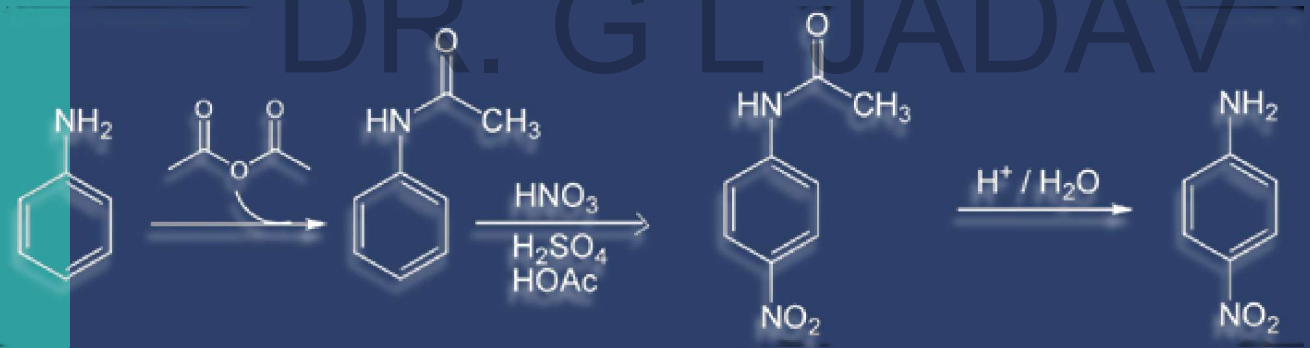
- ***Deactivation of –NH2 group called a protection of –NH2***
- ***Control the rate of reaction***
- ***Prevent formation of di/tri products***

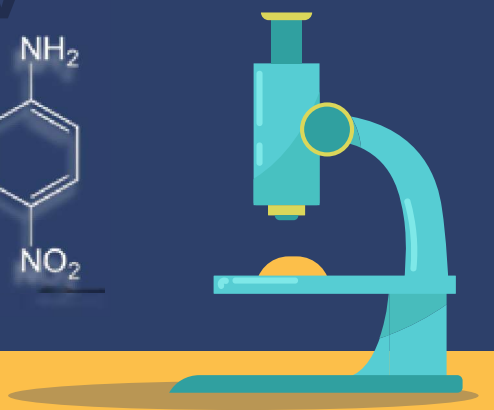




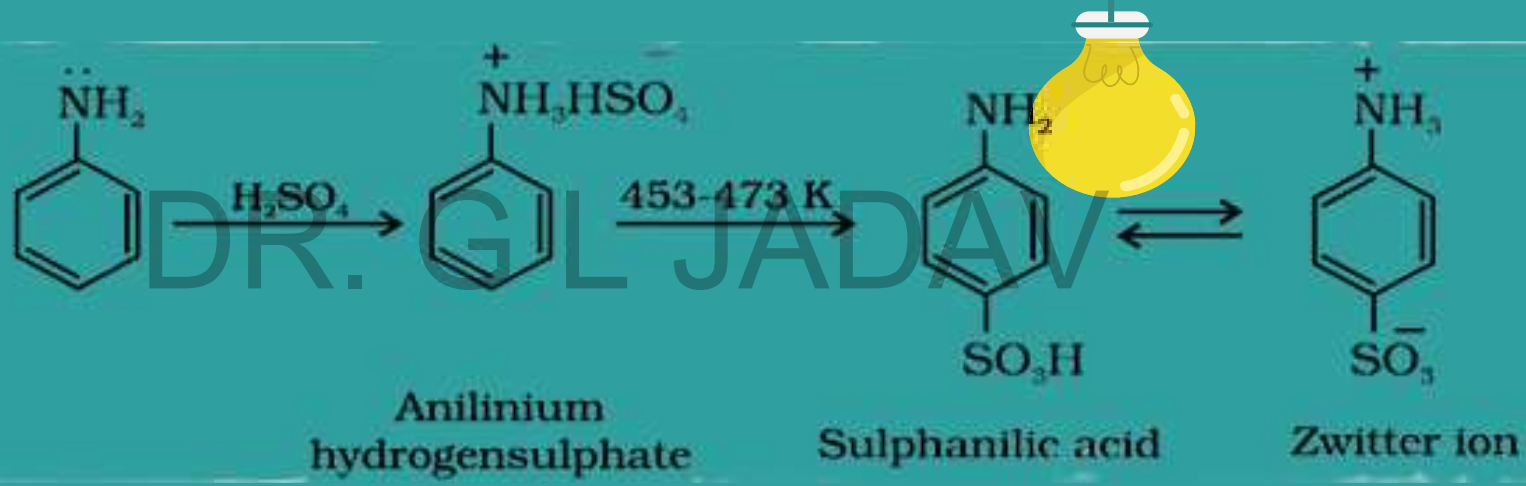
Nitration of aniline







Sulphonation of aniline



Separation of 1°, 2°, 3° amines

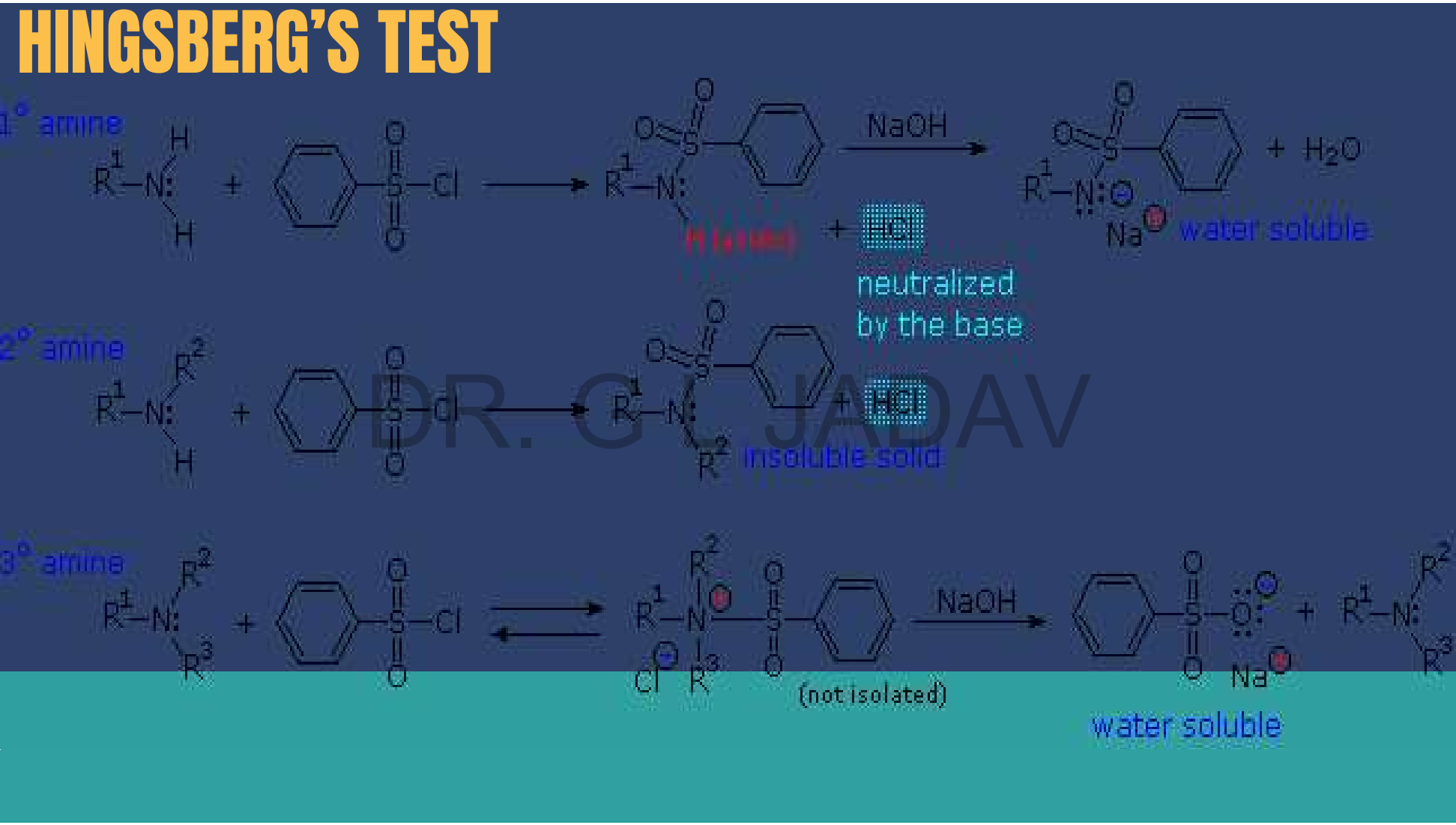
Hingsberg test

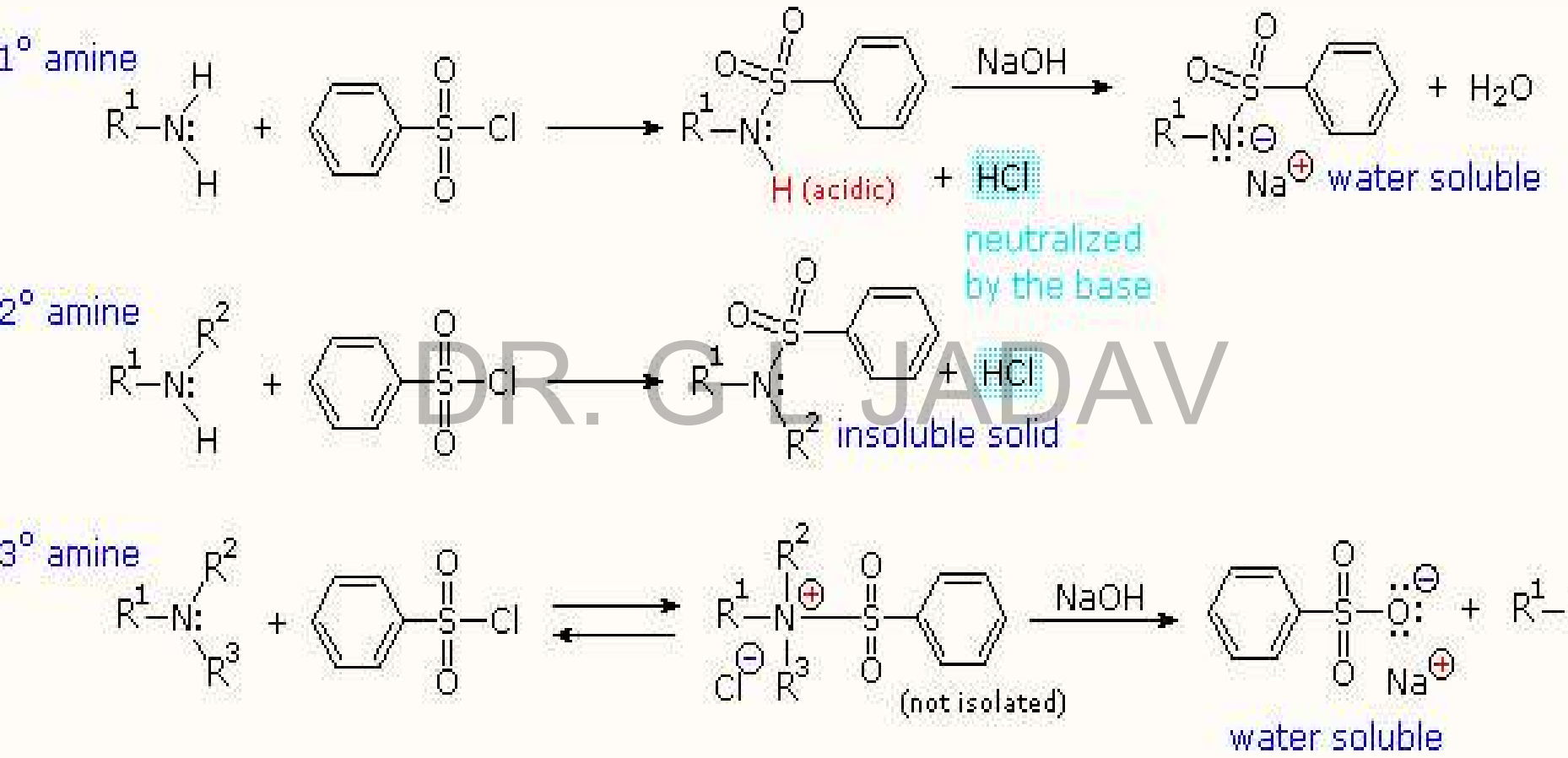
The amine is shaken with benzenesulfonyl chloride in the presence of aqueous KOH. Primary and secondary amines forms substituted sulfonamides while 3° do not react at all.

The mono substituted sulfonamide from 1° amine has an acidic ‘H’ attached to ‘N’. Reaction of KOH converts this amide into a soluble salt. Acidification of this solution regenerated the insoluble amine.

The disubstituted sulfonamide from a secondary amine has no acidic ‘H’ and remains insoluble in the alkaline reaction mixture.

HINGSBERG'S TEST



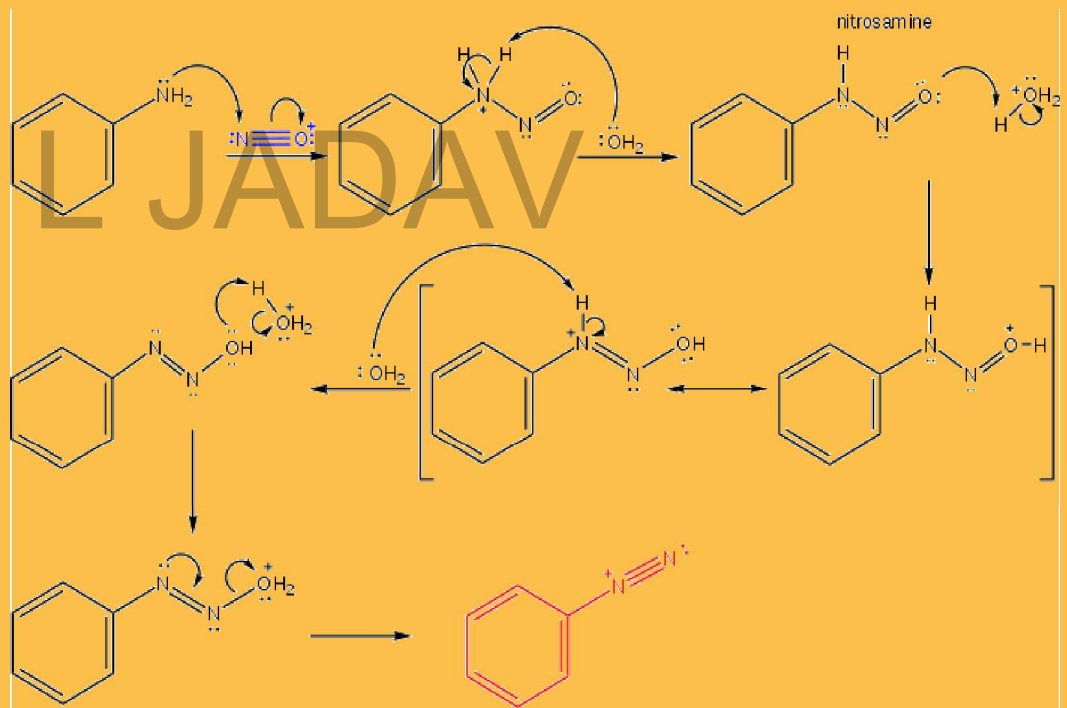

1° amine
NaOH
+ H2O
H (acidic)
+ HCl
neutralized
by the base
Na
water soluble
2° amine
+ HCl
insoluble solid
3° amine
NaOH
(not isolated)
water soluble

Aryldiazonium Salts

$$NaNO_2 + HCl \longrightarrow HONO + NaCl$$

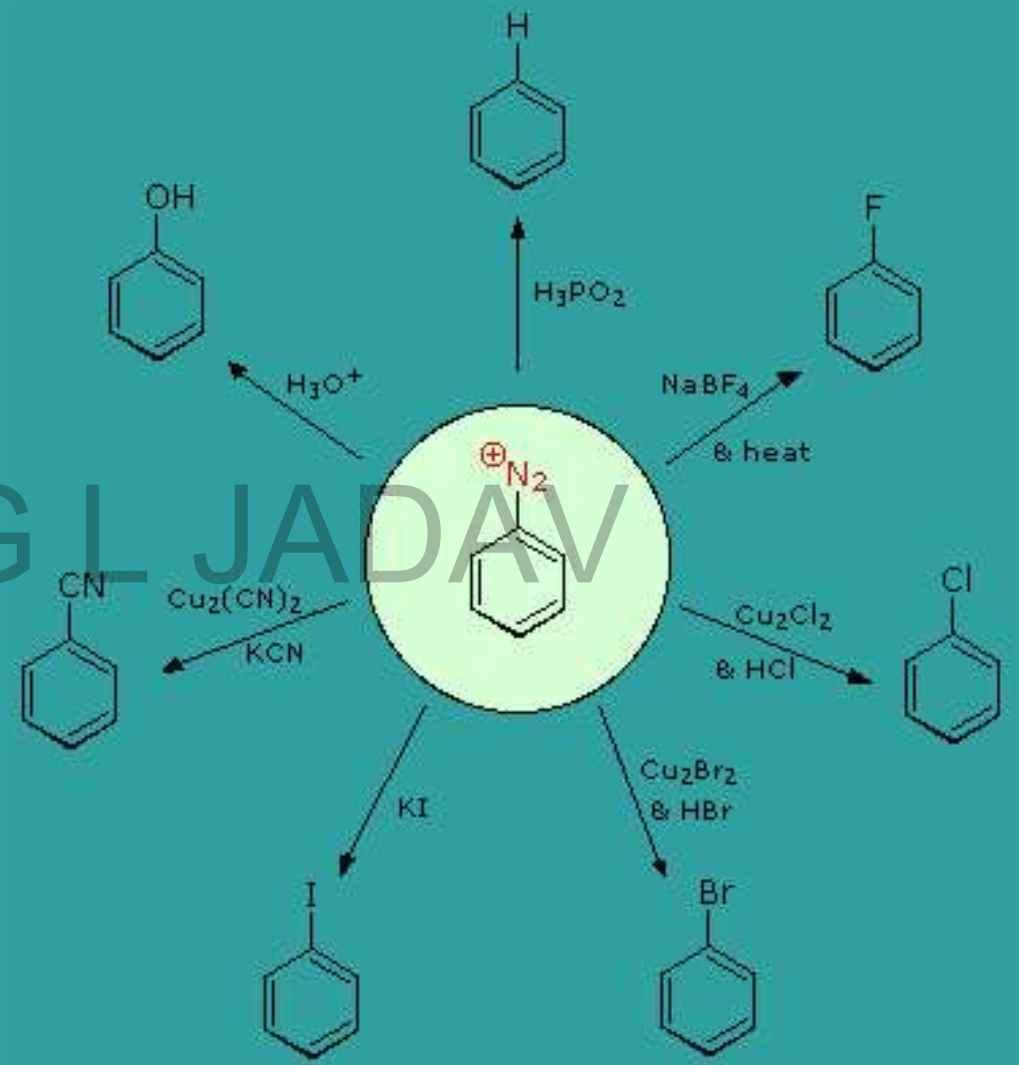
$$ArNH_2 + HNO_2 + HCl \xrightarrow{0\text{-}5\ ^oC} ArN_2^{\oplus}Cl^{\ominus} + 2H_2O$$

The process of converting an amine into the diazonium salt is called diazotization



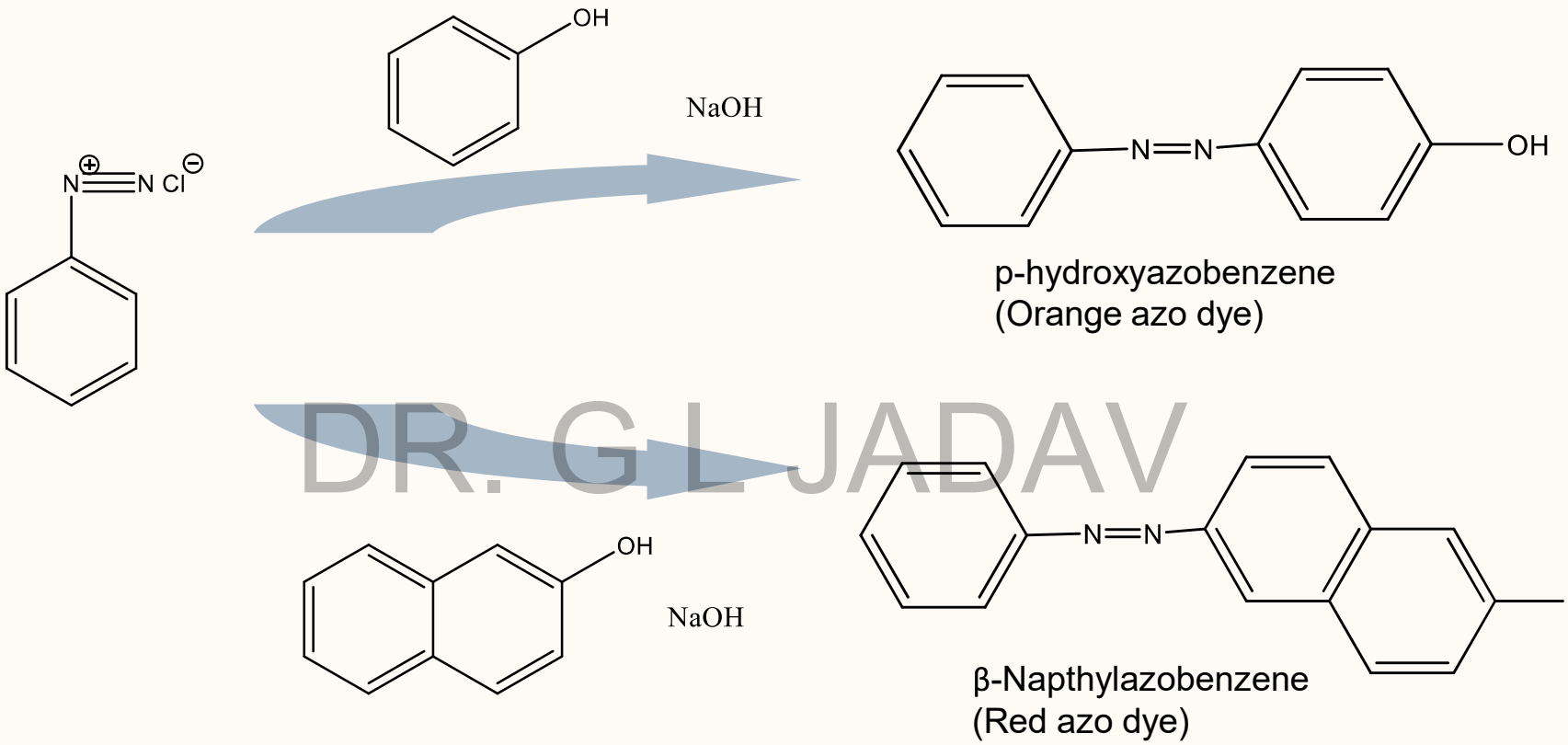
DR. G L JADAV

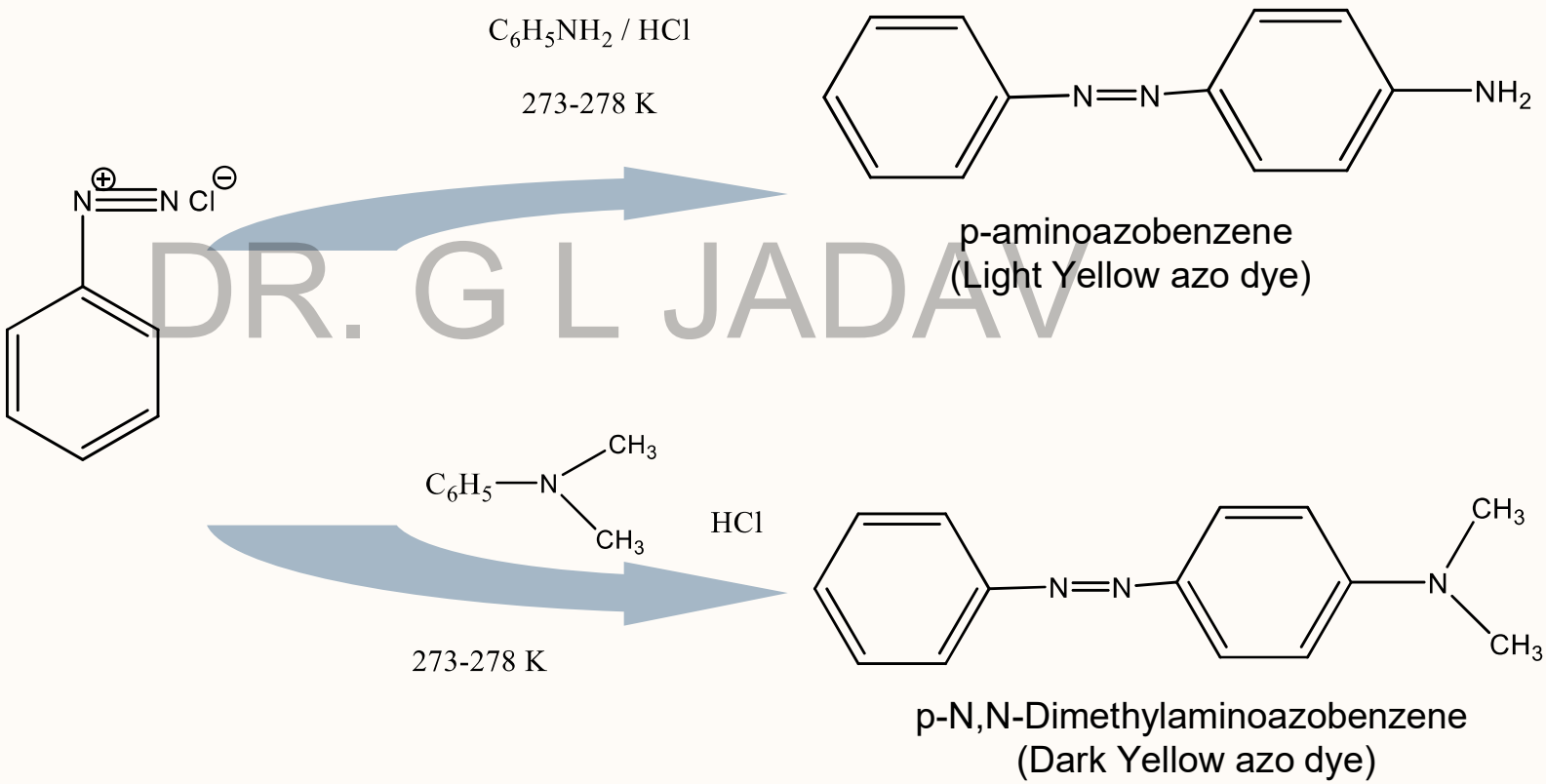
Reactions



Azo Coupling Reaction

- Phenolic substances when reacted with a diazonium chloride salts at lower temperature in NaOH solvent it produces orange – red colour products known as azo dyes
- Beta napthol in NaOH reacts with benzene diazonium chloride at 273-278 K temperature, orange and red colour dyes are obtained.
- Anline or N.N-dimethyl aniline when reacted with benzene diazonium chloride in Hydrochloric acid give Yellow dye.


OH
NaOH
N Cl
N=N
OH
p-hydroxyazobenzene
(Orange azo dye)
OH
NaOH
N=N
OH
β-Napthylazobenzene
(Red azo dye)


C6H5NH2 / HCl
273-278 K
N Cl
NH2
p-aminoazobenzene
(Light Yellow azo dye)
C6H5
CH3
CH3
HCl
273-278 K
CH3
CH3
p-N,N-Dimethylaminoazobenzene
(Dark Yellow azo dye)

Nitro Compounds

C H N & O atoms

R-NO2

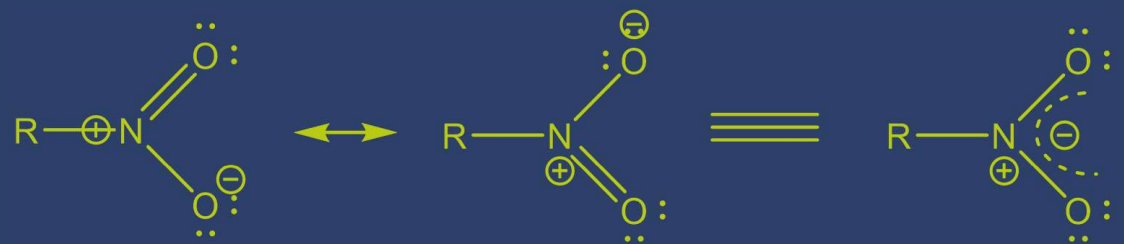
R= Alkyl or aryl

Nitro alkane

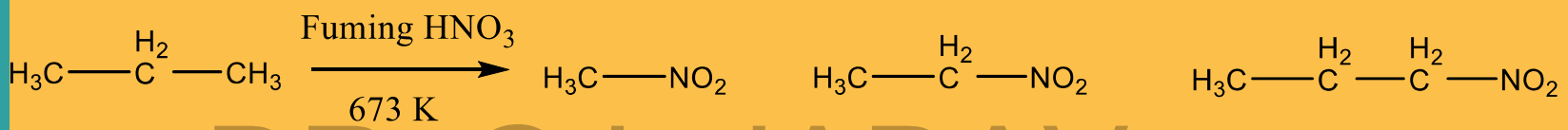
Nitromethane, Nitroethane etc

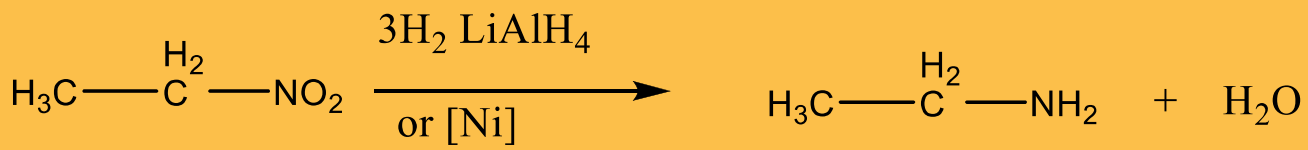
Nitrobenzene

Compouds are Neutral, colourless, sparingly water soluble and has odour.



Nitro Compounds





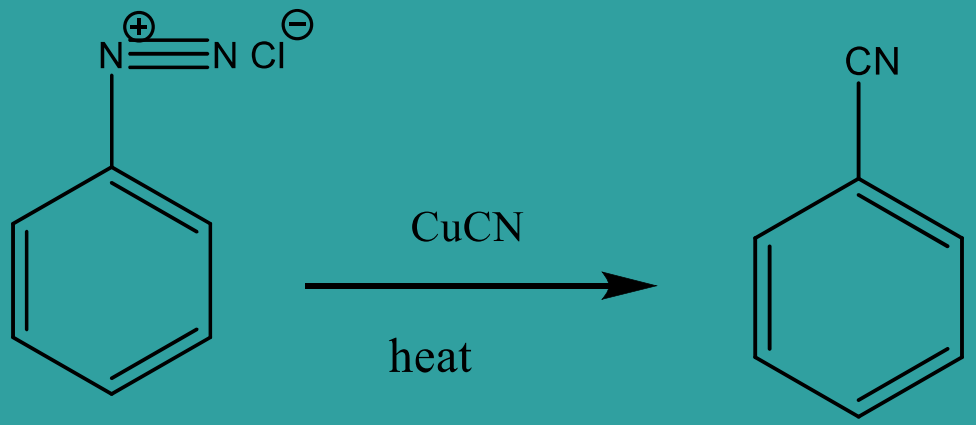
Cyanide/Nitrile

- C H N elements
- R – CN
- "Cyanide" as suffix in nomenclature
- CH3CN = Methylcyanide
- C2H5CN = Ethylcyanide

- IUPAC
- Longest chain of C atoms
- Suffix Nitrile
- CH3CN = ethane nitrile
- CH3 – CH2 – CN = propane nitrile

- Aromatic / cyclic substance, Suffix "Carbonitrile"
- Benzenecarbonitrile
- Cyclohexanecarbonitrile

Cyanide/Nitriles

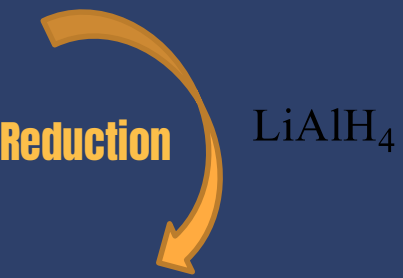


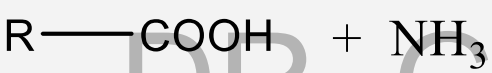
Preparation

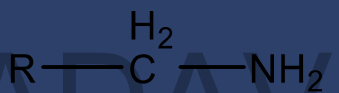
Diazoniium salt with cuprous cyaninde in KCN gives benzonitrile (cyanobenzene)

Sandmayer Reaction

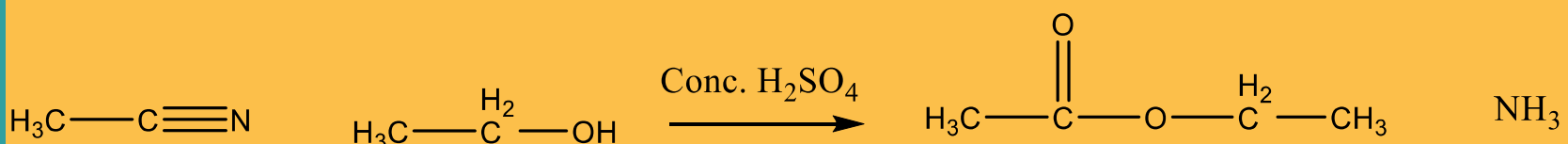
Reaction







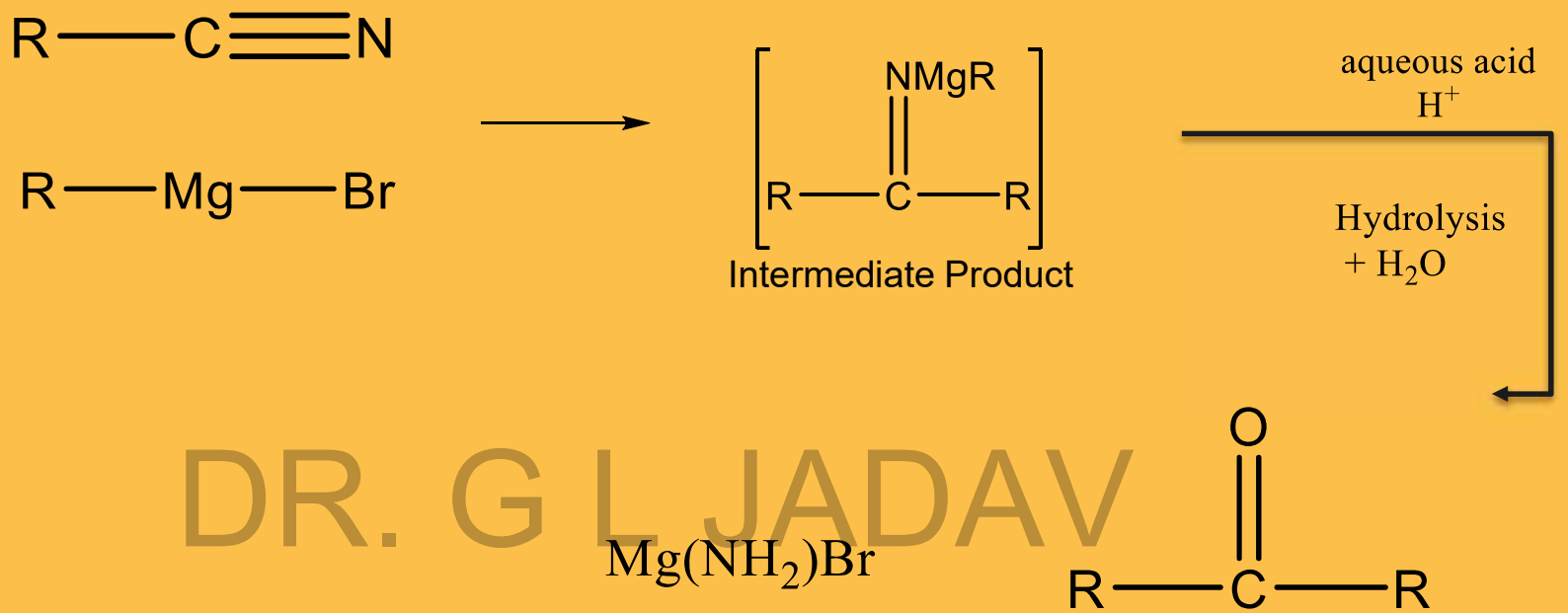
Ethylethanoate (ethyl acetate) is formed when ethane nitrile and ethanol are heated in presence of concentrated sulphuric acid



Cyanide on reaction with Grignard reagent produces an intermediate which upon acid hydrolysis results in a Ketone

With Grignard Reagent

A Grignard reagent or Grignard compound is a chemical compound with the generic formula R−Mg−X, where X is a halogen and R is an organic group, normally an alkyl or aryl.



Reaction

ISO CYANIDE COMPOUNDS

- Isonitrile / carbolamine
- C H N elements
- R-N≡C
- Dipolar, N is Positive charged and C Negative charged
- Characteristics opposite to cyanide
- Prefix “ISO” to the word cyanide
- IUPAC – CH3-NC ethaneiso-nitrile or methyl-carbylamine (Methylsiocyanide)

$$R\text{-}NH_2 + CH_3Cl + KOH \longrightarrow RNC + 3KCl + 3H_2O$$

Primary amine

Alkyl Isocyanide