

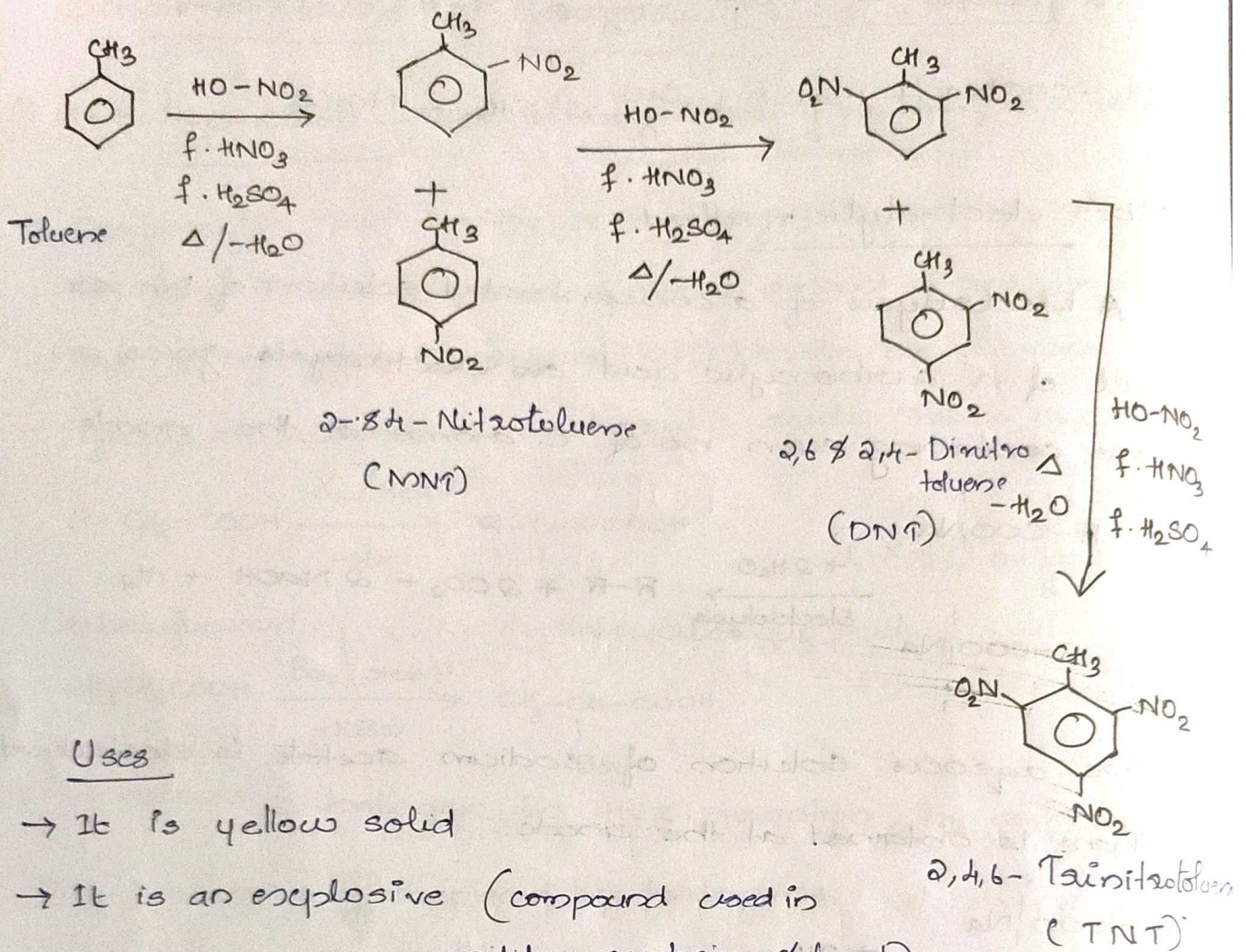
NITRO COMPOUNDS

- Compounds containing $-NO_2$ group.

(A) 2,4,6-Trinitrotoluene or TNT

preparation

- Prepared through continuous nitration of toluene by heating with a mixture of fuming HNO_3 & H_2SO_4 .



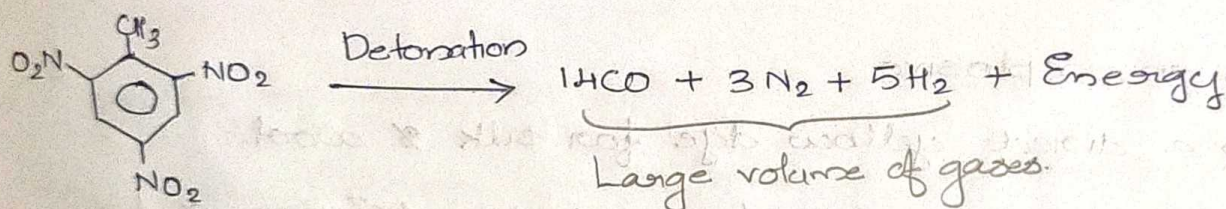
Uses

- It is yellow solid
- It is an explosive (compound used in military explosive & bomb & grenade)
- Used in industrial explosive (quarrying, deep well, underwater blasting)

- Stable & safely handled, can store for a prolonged periods without decomposition. Require detonation to set it off.
- Used as chemical intermediate in the manufacture of dyestuff & photographic chemicals.

Reason for explosive nature of TNT

- ① TNT contains 3 $-NO_2$ groups that are closely packed and they experience a mutual hindrance & thereby strain in the molecule. So an input of an energy in the form of heat/electricity (referred to as detonation) decompose the strained molecule in high speed reaction.
- ② The oxygen content of the strained TNT is sufficient to make itself oxidising upon detonation and the speed of the reaction release a large volume of gases and a large amount of energy all once, causing explosion.



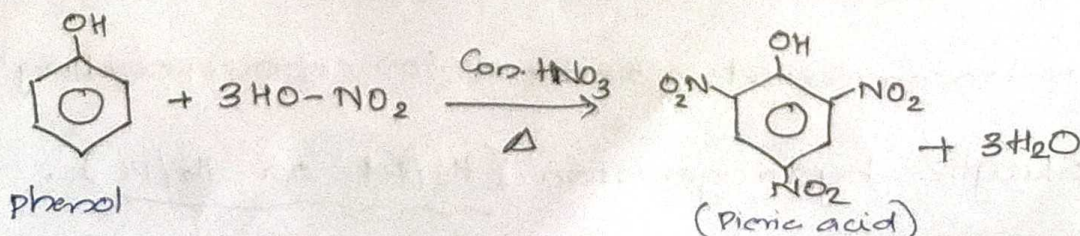
* 1 gm of TNT produce 1 l of gas, which is a 1000 fold increase in volume.

This expanding hot gas mixture can be used to propel a projectile (such as a bullet from a gun) or for demolition purposes.

(B) 2,4,6-Trinitrophenol / Picric acid

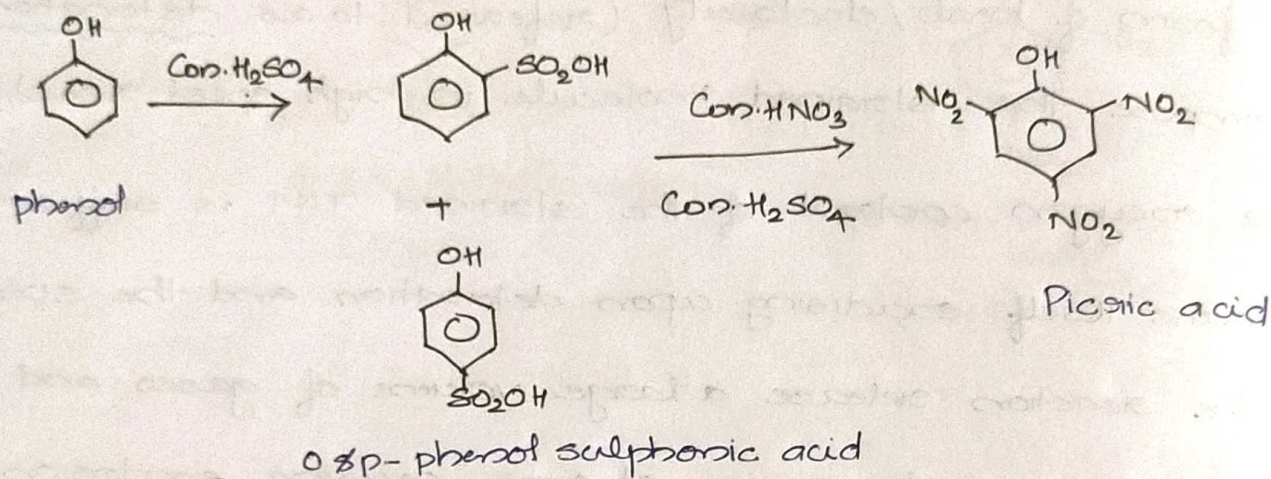
→ Direct nitration of phenol with con. HNO_3 alone or with the nitrating mixture (con. HNO_3 + con. H_2SO_4) yields

Picric acid



But here, the yield is low, because HNO_3 is strong oxidant

∴ Prepared by sulphonating phenol by heating with
con. H_2SO_4 to a mixture of o & p-phenol sulphonic acids
and then nitrating them using con. HNO_3 + con. H_2SO_4



Uses

- Used as an explosive
- Used as a direct yellow dye for silk & wool.
- As a laboratory reagent for detecting K^+ ions & for identification of polynuclear hydrocarbons.
- As an antiseptic for burns.

AMINES

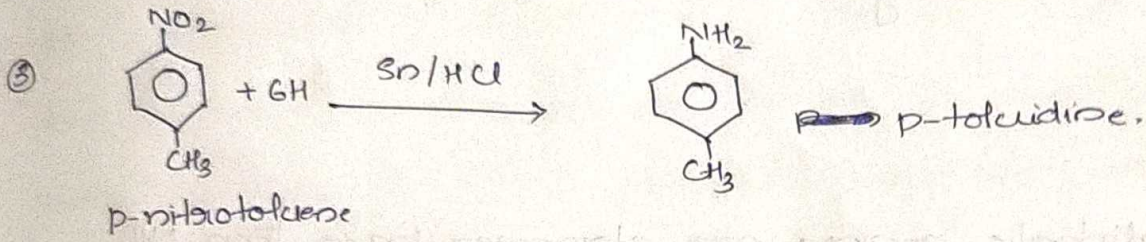
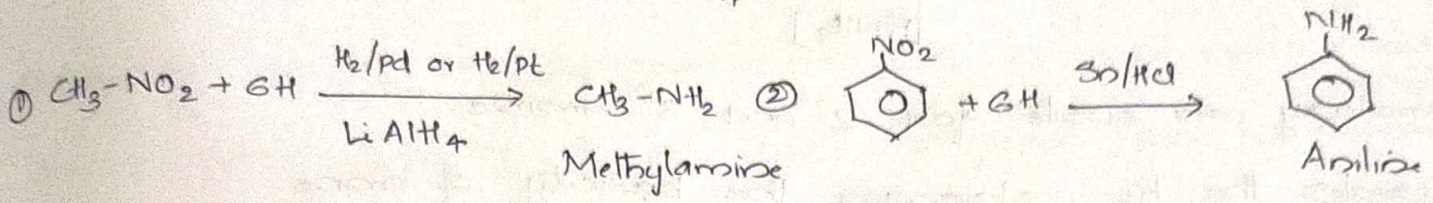
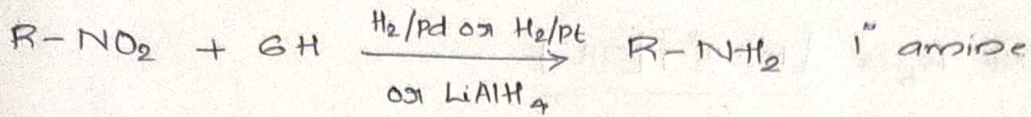
Organic derivatives of ammonia in which one / two / all
three H ~~is~~ are replaced by alkyl or acyl substituents.

Preparation

(1) By reduction of nitrocompounds

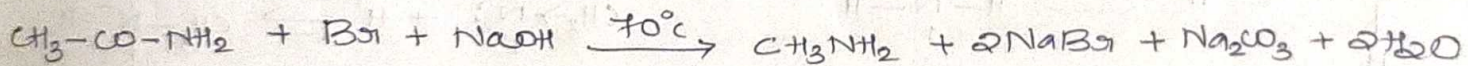
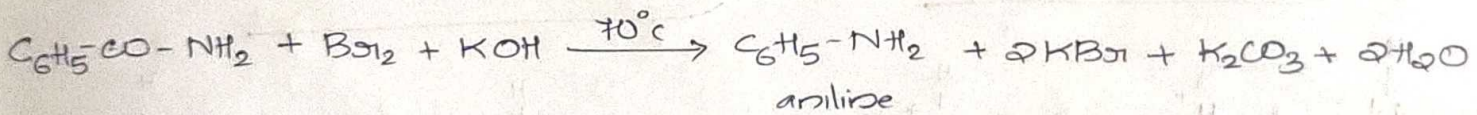
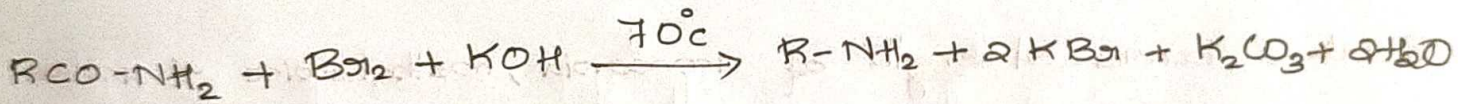
Nitrocompounds reduced to corresponding amines by
catalytic hydrogenation (H_2/Pd or H_2/Pt).

→ Reduced Nitro compounds are also reduced by reductants like Fe/HCl or Sn/HCl or LiAlH₄



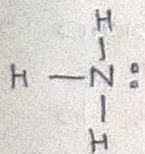
(2) By Hofmann's bromamide reaction

→ 1° amides on reaction with Br₂ and KOH / NaOH at about 70°C yield 1° amine. (having one 'C' less than parent amide)

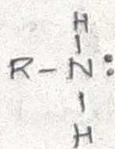


Basicity of Amines

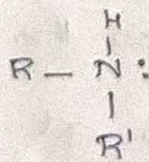
All three kinds of amines like ammonia, contain a lone pair of e⁻ on N atom & hence has the tendency to donate e⁻ & thereby act as bases.



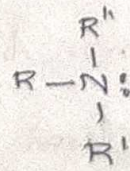
Ammonia



1° amine

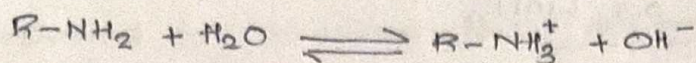


2° amine



3° amine

Consider the following equilibrium for a 1° amine in water.



$$\text{Basicity const } K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]}$$

Similarly, can write for 2° and 3° amine.

→ Greater the K_b , stronger the basicity of amine.

Table

From table

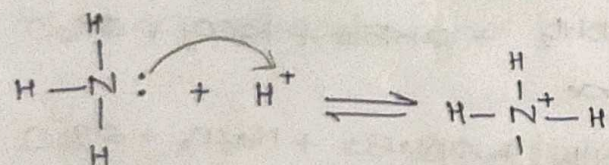
All type of aliphatic amines are stronger base than NH_3

(due to +I effect of R grp - more e^- in N)

Aromatic amines are weaker base than NH_3

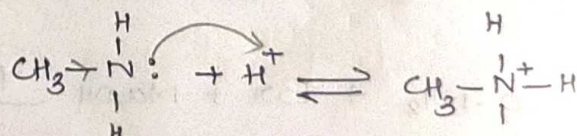
(due to e^- withdrawing nature of aryl grp - decrease e^- density on N)

Relative basic strengths of ammonia, methylamine & aniline



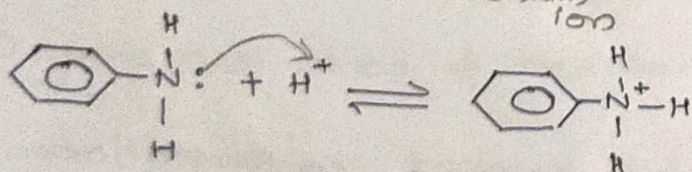
Ammonia

ammonium ion



Methylamine

Methylammonium ion

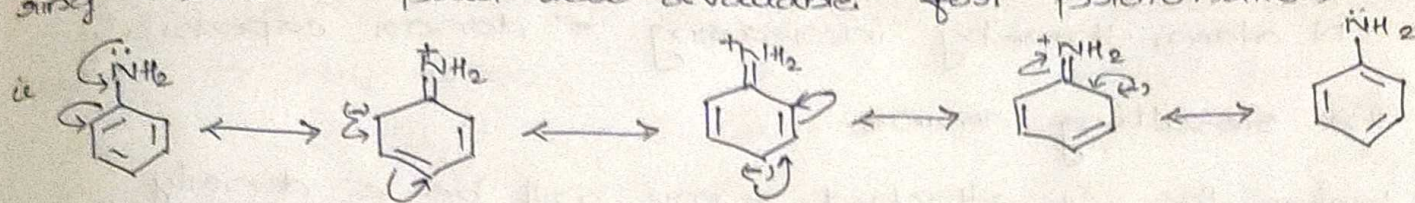


Aniline

Anilinium ion

In methylamine → +I effect of R group increase the e^- density on N atoms. And also the methylammonium ion formed from aniline amine get stabilised due to dispersal of +ve charge by +I effect of methyl group.

In aniline \rightarrow +R/+M effect of $-NH_2$ group attached to the ring make e^- pair less available for protonation.



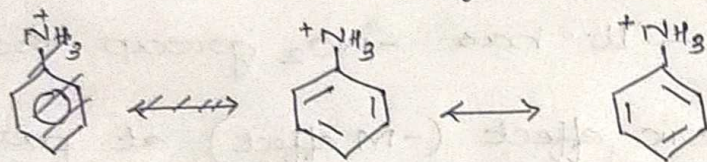
Due to above e^- delocalisation of 'N' lone pair over the aromatic ring, it is less available for protonation.

as compared to that in NH_3 or any aliphatic amine.

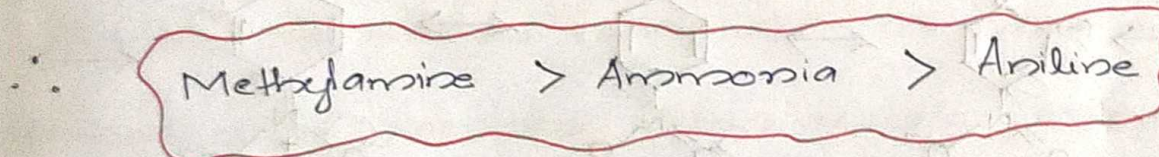
And small +ve charge on N repels the proton.

Hence aniline & other aromatic amines are less basic than NH_3 / aliphatic amines.

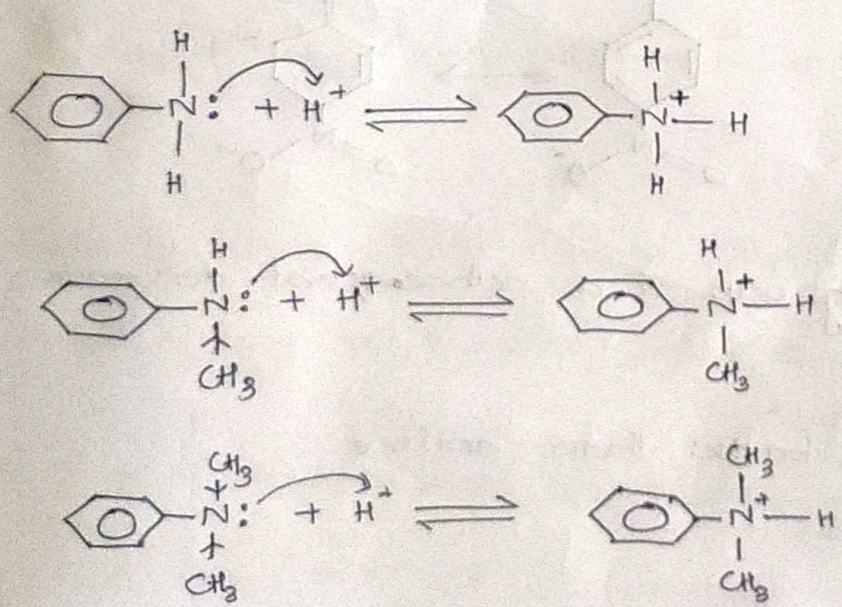
Further anilinium ion formed has only two resonance str.



So anilinium ion is not as stabilised through resonance as aniline.

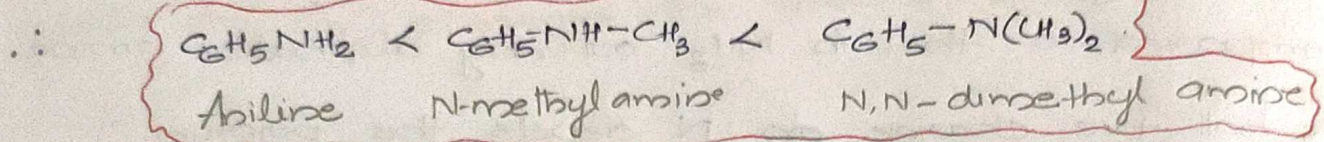


Relative basic strengths of aniline, N-methylaniline and N,N-dimethylaniline



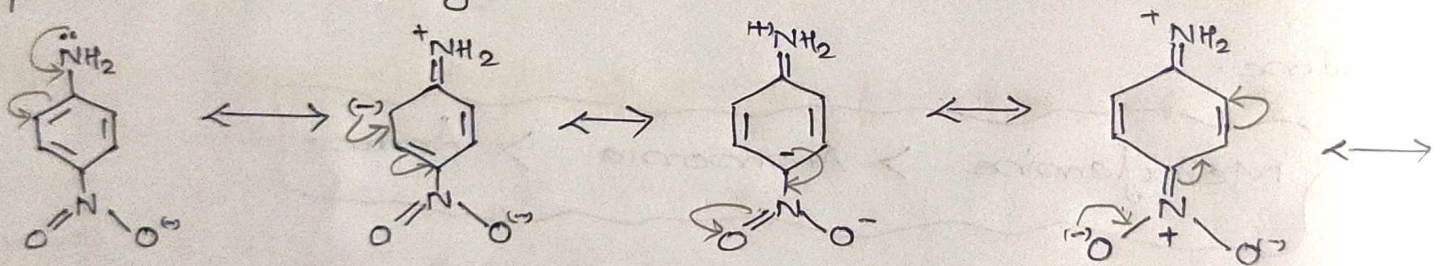
+I effect of alkyl group increases the e^- density on the N atom, thereby increasing e^- donor capability of the resulting amine.

So higher the CH_3 attached, more will be e^- density on N atom & more will be the basicity



Relative ^{basic} acid strengths of aniline, p-nitroaniline & p-anisidine.

In para-nitroaniline — It has $-NO_2$ group showing e^- withdrawing mesomeric effect ($-M$ effect) at para position to $-NH_2$ group.

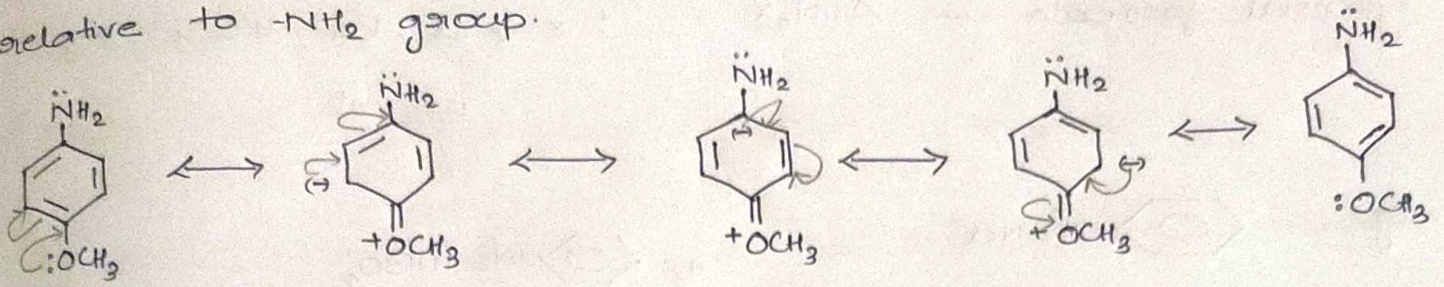


$-NO_2$ group withdraws e^- density, this cause a decrease in the electron

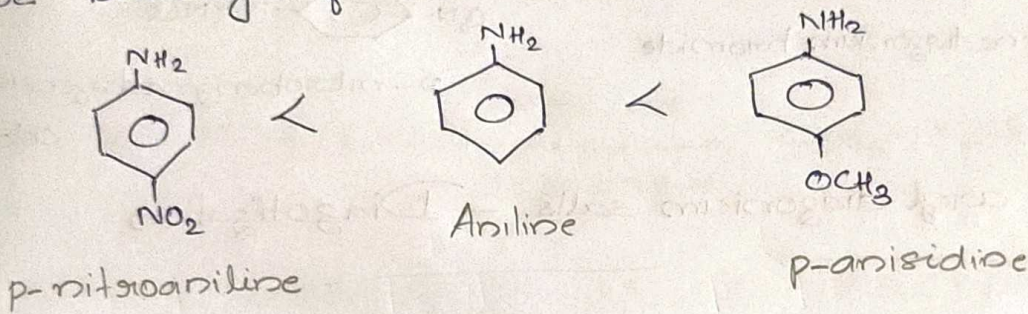
density on N atom of $-NH_2$ group & a subsequent decrease in the basicity of amine.

\therefore p-nitroaniline is less basic than aniline

In p-anisidine — It has $-OCH_3$ group showing e^- -donating mesomeric effect (+M effect) at para position relative to $-NH_2$ group.

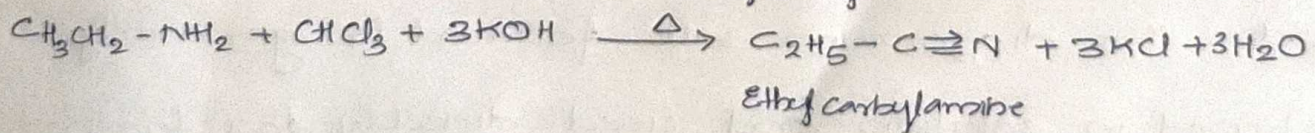
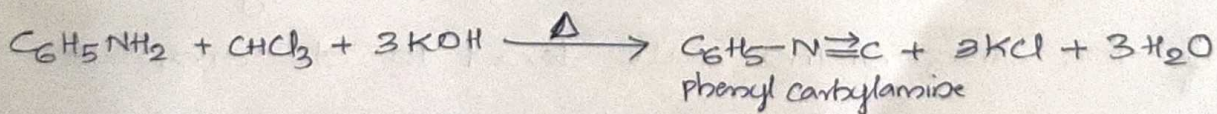
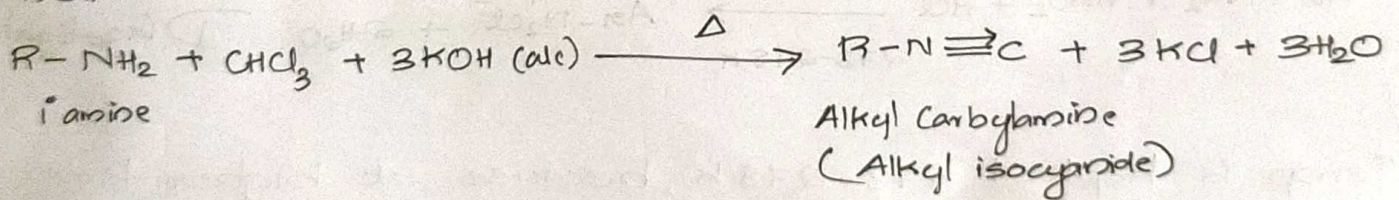


As $-OCH_3$ group release e^- density, this cause an increase in the N atom of $-NH_2$ group and subsequent increase in the basicity of the amine.



Carbylamine Reaction / Hofmann's Carbylamine Reaction

Aliphatic as well as aromatic primary amine when warmed with chloroform & an alcoholic solution of KOH yield corresponding carbylamine (isocyanides). It has foul smell.



2° & 3° aliphatic and aromatic amine \longrightarrow No Rxn

Test for 1° amine & to distinguish 1° amine from 2° & 3° amine