

Study Material: 2

Name- Sayanwita Panja

Discipline- B.Sc (H)

Subject- Chemistry

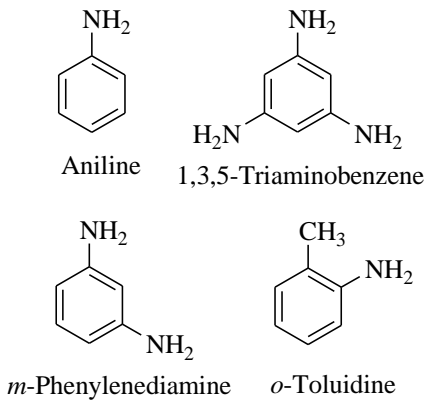
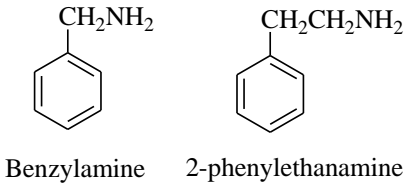
Semester- IV

Course Code- CC10

Topic- Organic Chemistry, Nitrogen Compounds

ORGANIC COMPOUNDS OF NITROGENS:

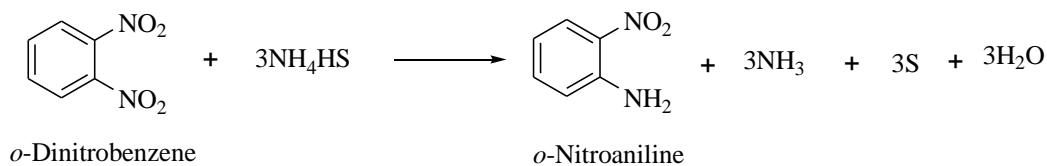
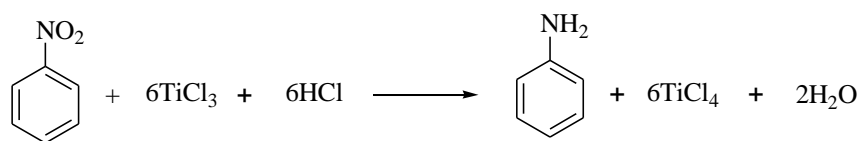
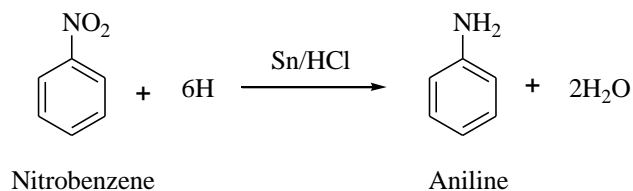
:Aromatic Amines:

Nuclear Substitution	Side Chain Substitution
Those in which -NH ₂ group is attached to the nucleus.	Those in which -NH ₂ group is joined to a carbon atom of the side chain.
 <p>Aniline 1,3,5-Triaminobenzene <i>m</i>-Phenylenediamine <i>o</i>-Toluidine</p>	 <p>Benzylamine 2-phenylethanamine</p>

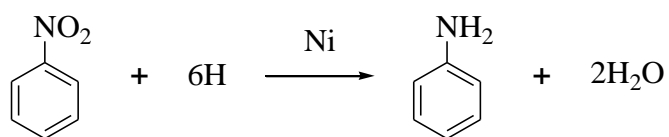
Methods of formation:

1. Reduction of nitro compounds:

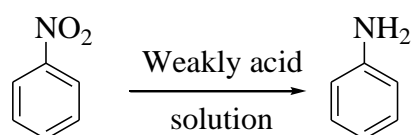
(a) Chemical reduction:



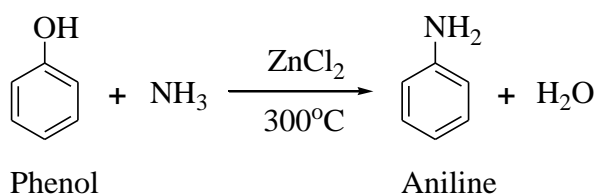
(b) Catalytic reduction:



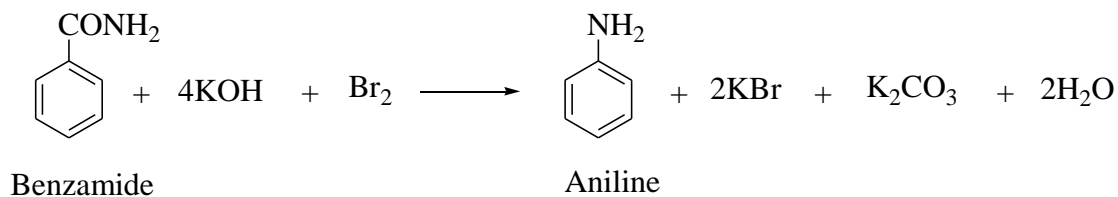
(c) Electrolytic reduction:



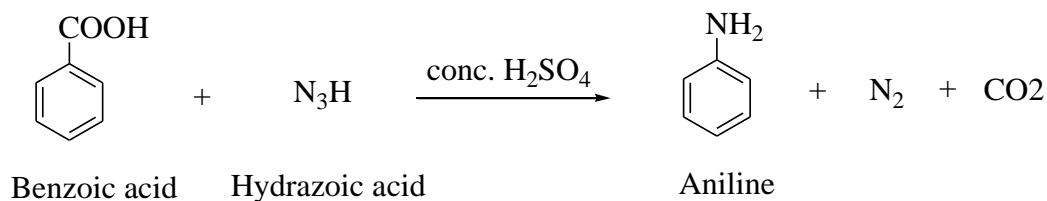
2. Ammonolysis of phenol:



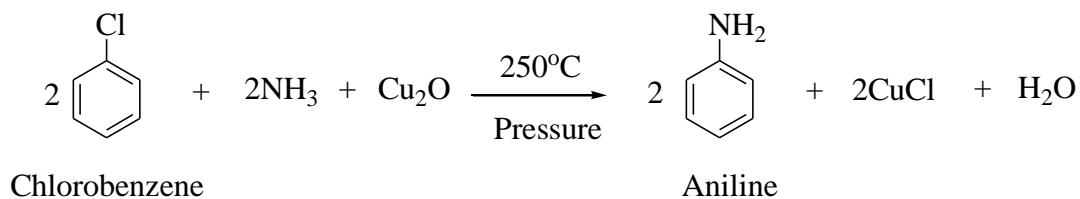
3. Hofmann method:



4. Schmidt reaction:

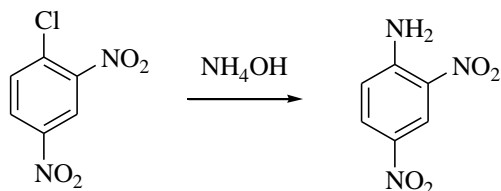


5. Ammonolysis of halogen compounds:

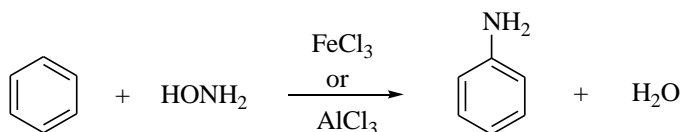


Sayanwita Panja/ B.Sc/ Chemistry (H)/ Sem-IV/ CC10/ Nitrogen Compounds

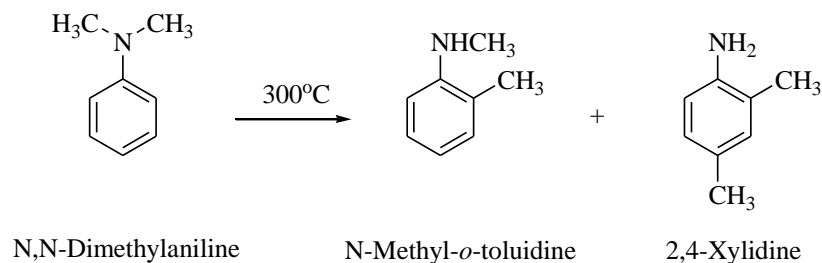
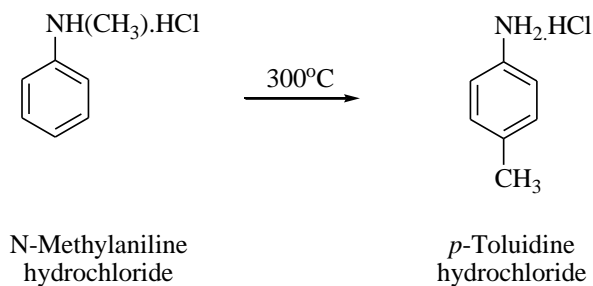
When electron withdrawing groups like $-\text{NO}_2$, $-\text{SO}_3\text{H}$, $-\text{CN}$ etc. are present in *o* and *p* positions the reaction takes place even with aqueous ammonia.



6. Action of hydroxylamine with hydrocarbon:

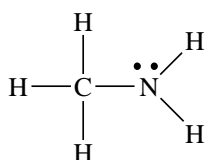


7. Isomerisation of alkyanilines (A.W. Hofmann):

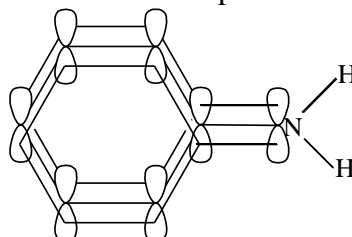


• Basic Character of Aromatic Amine:

The basicity in aromatic amines arises due to the presence of a lone pair of electrons at nitrogen. Since this lone pair of electrons is in conjugation with the π -electrons of the ring, it interacts with them and gets delocalized. Hence it is less available for co-ordination with a proton. In case of aliphatic amines, the lone pair of electrons at nitrogen is localized and hence readily available for protonation. As a result, aromatic amines will be less basic than aliphatic amines.

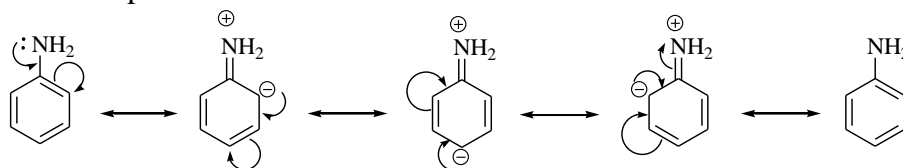


Methylamine

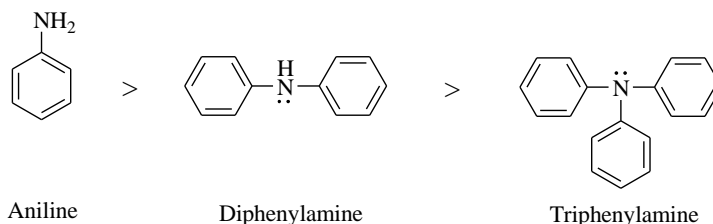


M.O. Picture of aniline
(delocalisation of lone pair of electrons
of nitrogen with the ring)

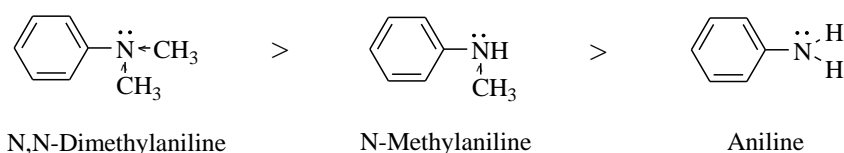
According to resonance concept the lone pair of electrons of nitrogen in aromatic amines, is in conjugation with the double bonds of the ring. The molecule, therefore, is a hybrid of resonance contributing structures having positively charged nitrogen. This +R effect of the amino group makes the electron pair less available at nitrogen. Hence the tendency of aromatic amines for protonation is hindered resulting in their decreased basic character as compared to aliphatic amines where no such factor operates.



In case of secondary and tertiary aromatic amino compounds the lone pair of electrons on nitrogen is delocalized towards two or three benzene rings hence they will be still weaker bases than aniline.

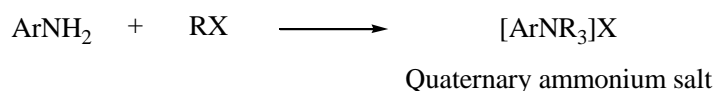
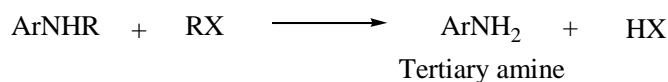
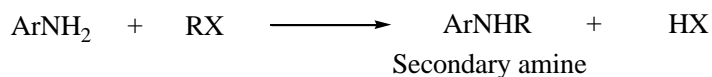


The presence of electron releasing substituent on nitrogen e.g. methane group in N-methylaniline would increase the basic character and therefore this would be a stronger base than aniline but weaker than N, N-dimethylaniline.

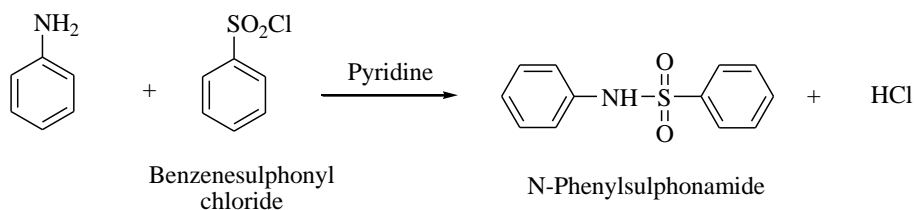
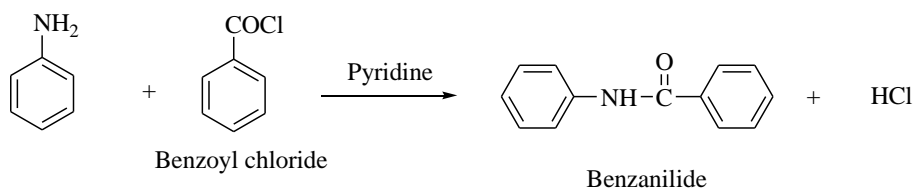
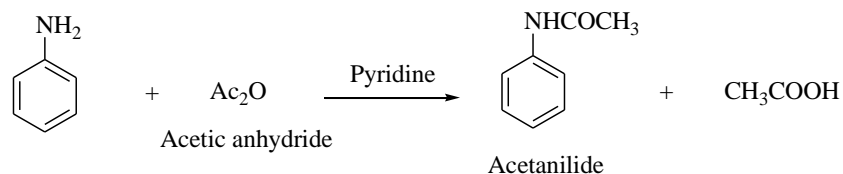
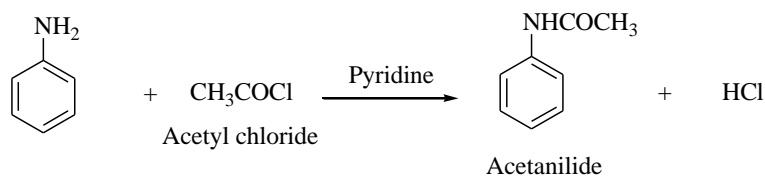


• **Reaction of Aromatic Amine:**

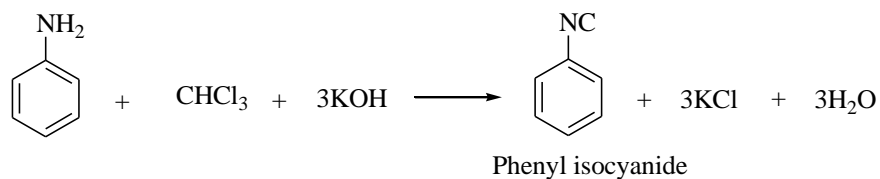
1. Reaction with alkyl and aryl halide:



2. Acylation:

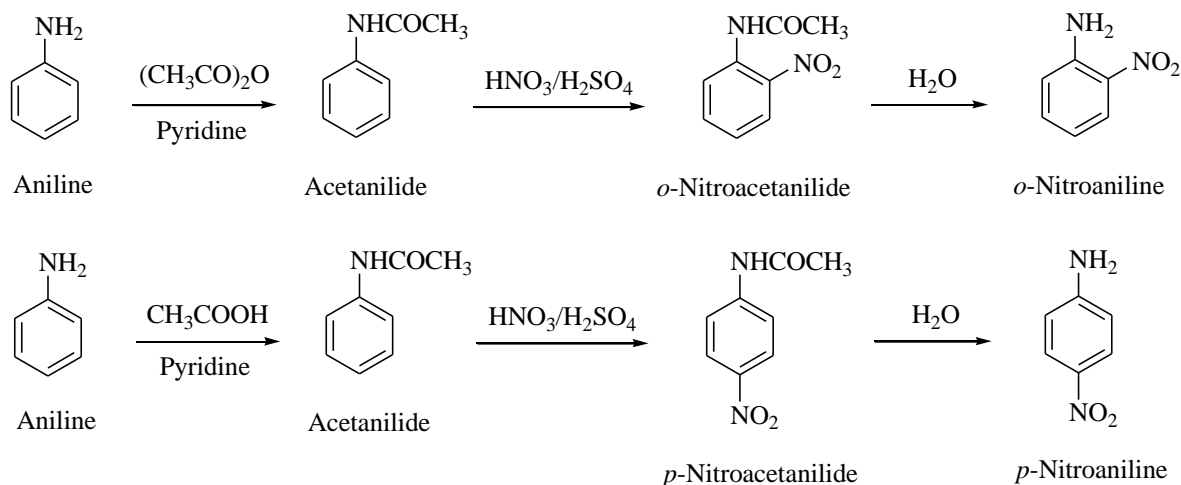


1. Carbylamine Reaction:

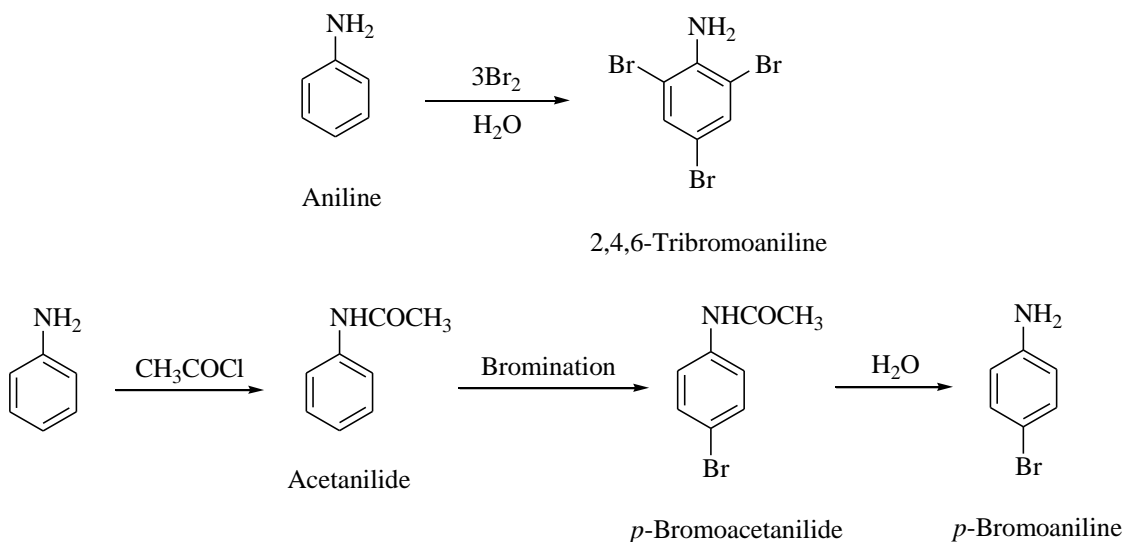


2. Nitration:

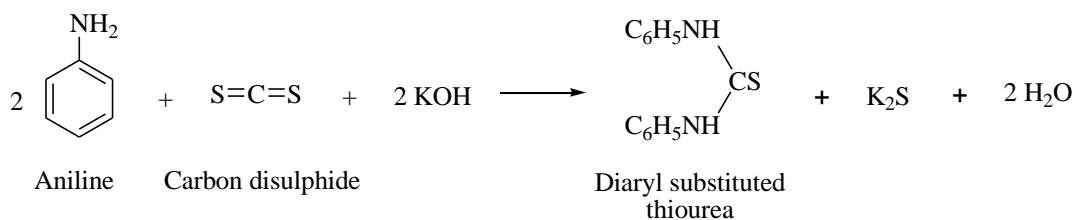
When acetic anhydride is used as an acetylating agent the product on nitration is mainly the *o*-nitroacetanilide whereas in case of acetic acid as acetylating agent the nitration product is mainly the *p*-isomer.



3. Halogenation:



4. Reaction with carbon disulphide:



More reactions of aromatic amine:

