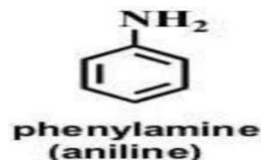


AROMATIC AMINES

- Aromatic amines have an amine group (-NH₂) attached directly to the Aromatic ring.
- Aromatic amines known as aryl amines .
- Example –



A.1 BASICITY OF AMINES -

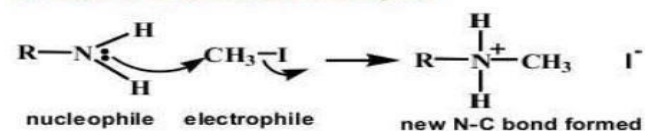
Amines can act as:

- a nucleophile (a Lewis base) because its lone pair none bonding electrons Can form a bond with an electrophile.
- a Brønsted-Lowry base because it can accept a proton from a proton acid.

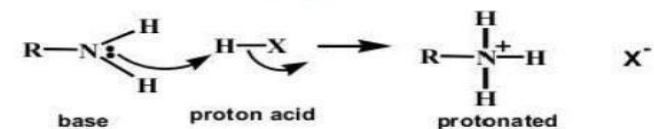
Factors That Affect the Basicity of the Amines

Amines are basic because they possess a pair of unshared

Reaction of an amine as a nucleophile



Reaction of an amine as a proton base



electrons, which they Can share with other atoms. These unshared electrons create anelectron density Around the nitrogen atom.

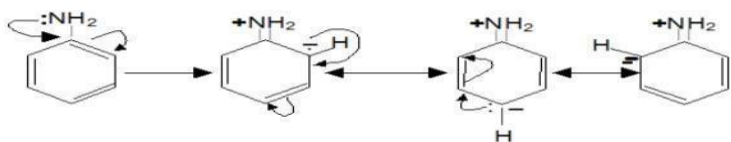
- The greater the electron density, the morebasic the molecule.
- Due to this property of the alkyl group (electron-donating group such as CH₃- andCH₃CH₂-) attached to the nitrogen of the amine, the electron Density around the nitrogen atom increases and its electron releasing Ability increases too.

- Due to the greater and easier release of electrons in the alkyl amine, the molecule becomes more basic than ammonia.
- The order of basicity: $3 > 2 > 1 > \text{NH}_3$
- the decreasing order of basicity will be: Primary amine > secondary amine > tertiary amines.

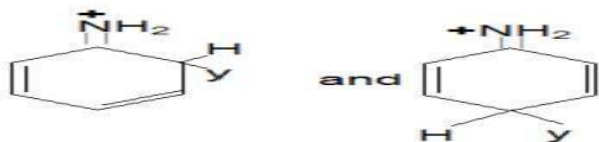
A.2 EFFECTS OF SUBSTITUENTS ON BASICITY -

Ring Substitution in Aromatic Amines

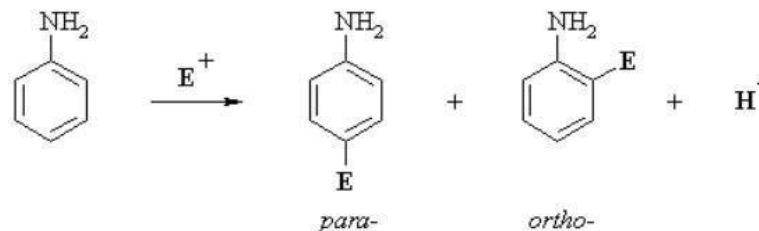
- The $-\text{NH}_2$, $-\text{NHR}$ and $-\text{NR}_2$ are benzene activating groups through resonance effect of nitrogen where the lone pair of electron of nitrogen is shifted to the benzene ring making ortho and para positions available for electrophilic attack.



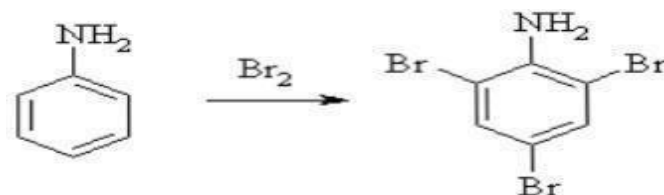
- The carbocation formed as intermediate are



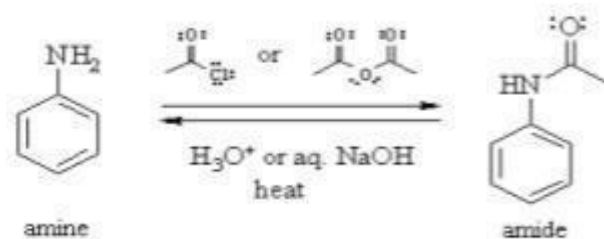
- Electrophilic Aromatic Substitution of Aryl Amines



- Polysubstitution can also be a problem. For example, bromination is very rapid, even in the absence of a catalyst, leading to bromination in all available ortho- and para-positions:



- To avoid these problems, it is customary to "protect" aryl amines as their N-acyl derivatives. The protecting group (an amide) can later be removed by either acid or base



hydrolysis.

- The amide is a less powerful activating group than the simple amino group, -NH_2 since resonance within the N-acetyl group of the amide competes with delocalization of the N lone pair into the ring and Steric effects in the amide also often lead to a decrease in the amount of the ortho-products.



- The group -NHCOCH_3 is less powerful ortho and para director because of the electron-withdrawing character of Oxygen makes nitrogen a poor source of electrons. This fact is made use in preparing mono substituted aniline. The -NH_2 group is such a powerful activator, that substitution occurs at all available ortho and para positions of aniline. If, however, -NH_2 group is converted to –

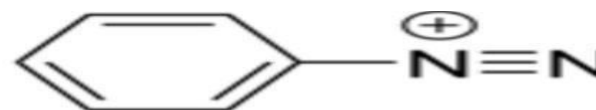
NHCOCH_3 , the molecule becomes less powerful activator. Hence only Mono substitution products are obtained. Finally -NHCOCH_3 is converted back to -NH_2 by

- hydrolyzing with Acid. This technique is especially used while nitrating aniline as strong oxidizing agent destroys the highly reactive Ring.

A.3 SYNTHETIC USES OF ARYL DIAZONIUM SALTS -

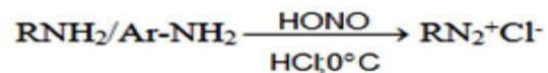
Diazonium compounds or diazonium salts are a group of organic compounds sharing a common functional group $\text{R-N}_2^+\text{X}^-$ Where R can be any organic group, such as an alkyl or an aryl, and X is an inorganic or organic anion, such as a halogen.

These Aryl diazonium salts are prepared by treating a primary amine with NaNO_2 in presence of conc. HCl ; the Temperature being 0°C .



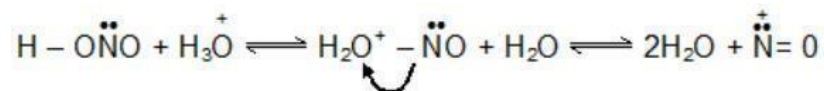
Benzenediazonium cation.

GENERAL REACTION -

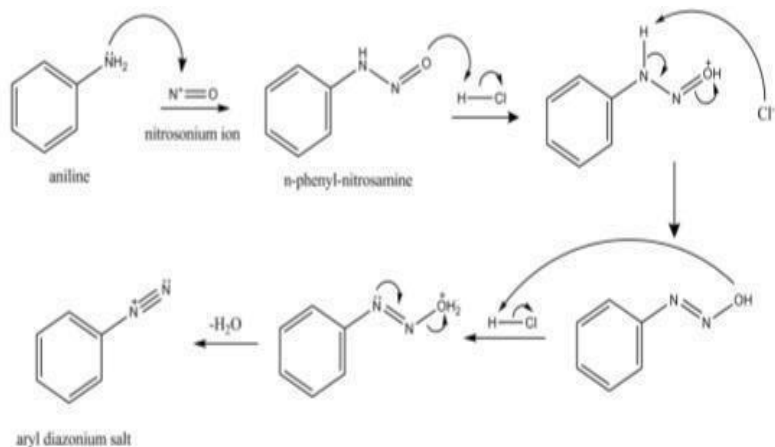


MECHANISM FOR DIAZOTIZATION:

STEP I:



STEP II:



REFERENCES :-

- 1) Textbook OF ORGANIC CHEMISTRY ARJUN BAHL& B SBAHL 17TEEN EDITION , PAGE NO. [670-679]
- 2) S.K GOSH TEXT BOOK OF ORGANIC CHEMISTRY CENTRALPUBLICATION PAGE NO. [795-868]
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PREPARED BY:- 1) MS. DESALE POOJA (14)

2) MS.GHARAT PRITI (21)

3) MS.FODSE SANIKA (18)

GUIDE BY:-MRS. CHIWADSHEETI N.S. (ASSISTANT PROFESSOR)

SUBJECT:- PHARMACEUTICAL ORGANIC CHEMISTRY-
II

CLASS:- SECOND YEAR B.PHARM

ACADEMIC YEAR:- 2021- 2022

