Chapter (II) : Amines

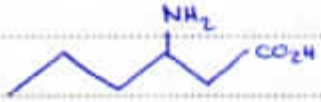
* Naming :

CH_3NH_2 — 1°

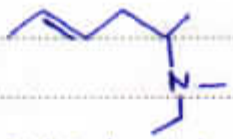
$CH_3-\underset{H}{N}-CH_3$ — 2°

$CH_3-\underset{CH_3}{\underset{|}{N}}-CH_3$ — 3°

trans-2-amino cyclopentanol.



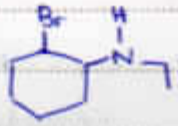
3-amino hexanoic acid.



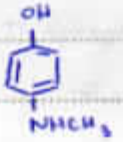
5-(ethyl methyl amino)-2-hexene.

* no priority for amine group.

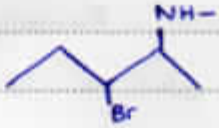
4-N-methyl amino-2-pentanone



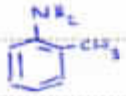
2-Bromo-2-ethylaminocyclo hexane



4-n-methyl aminophenol

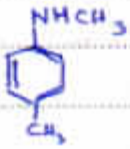


3-bromo-2-methylamino pentane
(least possible number)



o-methyl aniline

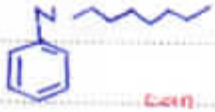
* any substituent other than $-OH$, $-\overset{O}{\overset{\|}{C}}-OH$, $-\overset{O}{\overset{\|}{C}}-H$, $-\overset{O}{\overset{\|}{C}}-$ it will have priority over it (in the aromatic)



4-methyl-N-methyl aniline

N,N - dimethyl aniline

* even if the chain was long (>6) we consider it aniline



can be named : - N - heptyl aniline

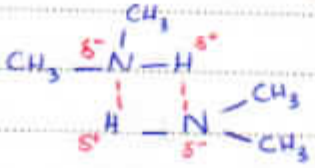
- N - phenylamino heptane

* Physical properties

- Boiling points:

alkanes < amines < alcohols

* they have weaker hydrogen bonding than alcohols



* Factors :

[1] Hydrogen bonding

$CH_3CH_2CH_2NH_2 > CH_3CH_2NHCH_3 > CH_3-\underset{CH_3}{N}-CH_3$

1° 2° 3°

* same number of carbons :

1° > 2° > 3° ⇒ more hydrogen bonding

Ex: Change from 1° → 2° < 12° (chemp) [2] Number of carbon atoms

from by addition of 1 carbon more carbon atoms higher boiling points

30° change $CH_3CH_2NH_2 > CH_3CH_2CH_2NH_2$

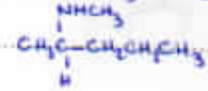
- Solubility :

high solubility in water due to hydrogen bonding.

Continuation to naming :

$CH_3CH_2NH_2$: ethyl amine or amino ethane

CH_3NHCH_3 : ethyl methylamine or methyl amino ethane (considering amino is the substituent)

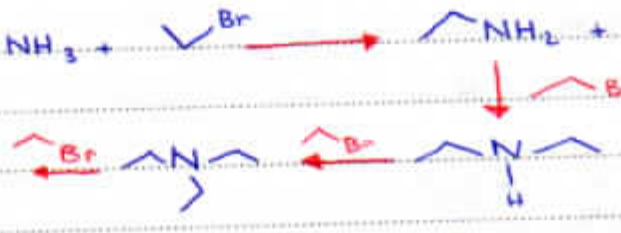


: 2 - N - methyl amino pentane

↳ to show that the methyl is connected to the (N)

No. Chapter(11)

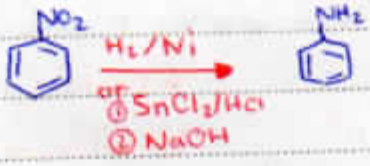
11.4 : Preparation of amines.



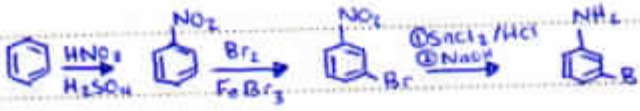
Intramolecular

* Synthetic methodologies :

[1]

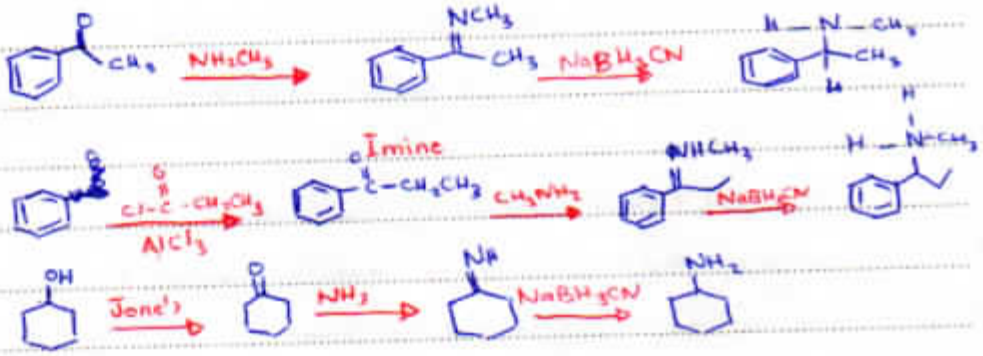


Synthesis



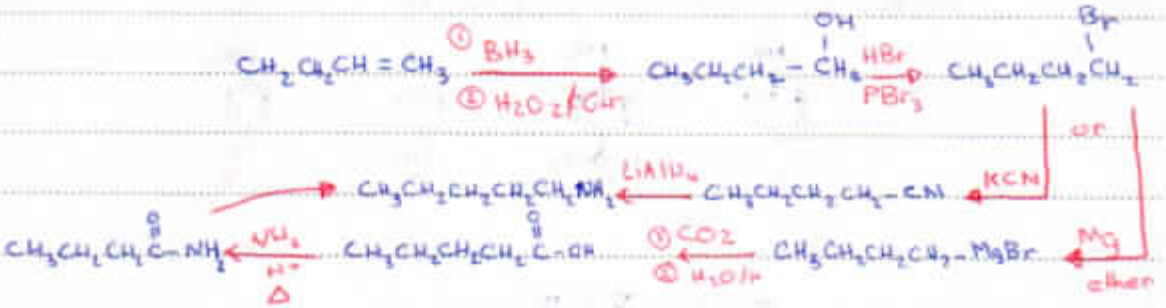
[2] $CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2NH_2$

[3]



Reduction of cyano compounds

$$R-C\equiv N \xrightarrow[LiAlH_4]{Li/H_2} R-CH_2NH_2$$



Bacisty of amines

$$H_2O + R-NH_2 \rightleftharpoons R-\overset{\oplus}{N}H_3 + OH^-$$

conjugate acids

amines: pKa ≈ 11

$CH_2\ddot{N}H_2$ $(CH_3)\ddot{N}H$ $(CH_3)_3\ddot{N}$

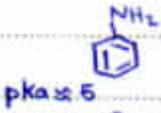
as a base $3° > 2° > 1°$ * supposed to be like this *

conjugate Acids:

pKa : 10.64 10.71 9.77.

$2° < 1° < 3°$ ⇒ bacisity: $3° < 1° < 2°$

amonia weakest base.

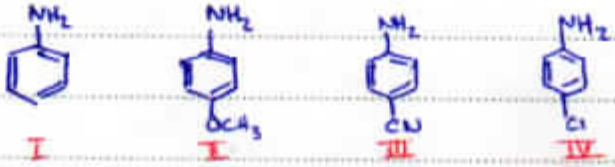

pka ≈ 5


stronger as a base (localized charge)

delocalization of electrons → weaker base

Basicity → 2° > 1° > 3° > amonia > anilines > amides

Q/ Rank this molecules according to bacisity



II > I > IV > III

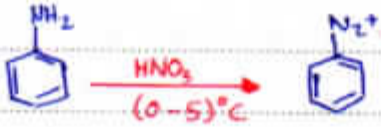
* amides are the weakest bases due to resonance effect :

↳ Most stable so the electrons spend more time in the double bond → Weaker base

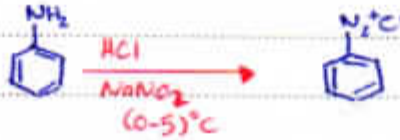
* What applies on amines applies on amides and anilines

Bacisity : 2° > 1° > 3°

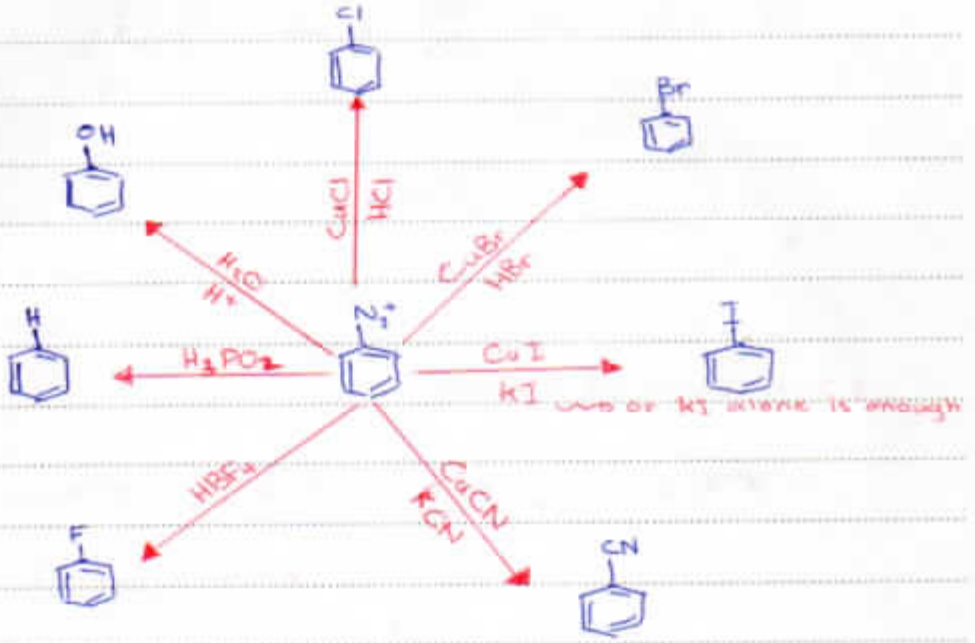
11.12 : Diazonium Salt :



phenyldiazonium



phenyl diazonium chloride

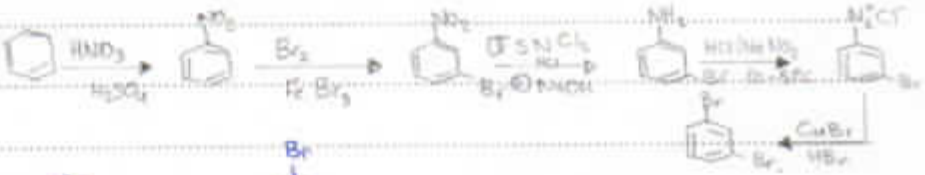


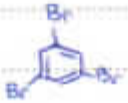
all the reactions

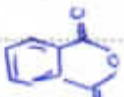
Synthesis 8

[1] Starting from NH_2 prepare CO_2H

[2] Starting from prepare 



[3] Starting from prepare 

[4] Starting from  prepare 

*Very Important Reactions

* always para to the substituent

azo compounds Dyes