كلية العلوم التطبيقية
Faculty of Applied Sciences

UMM AL-QURA UNIVERSITY

قسم الكيمياء
Department of Chemistry

Aromatic Amines

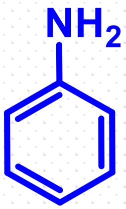
Chapter 8

COURSE NAME: **Chemistry of Aromatic Compounds**
COURSE CODE: **4022142-3**

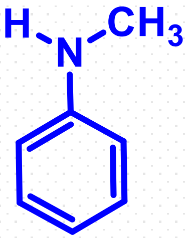
By the end of this chapter, you should understand:

1. How the amino group can be introduced into aromatic molecules.
2. The reactions of the amino group.
3. The basicity of amines.
4. The reactions of diazonium salts.

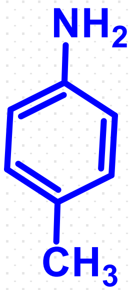
Nomenclature



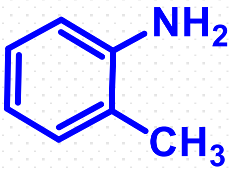
Aniline



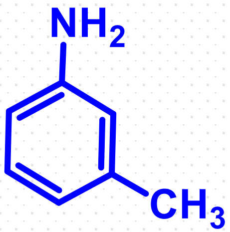
N-Methylaniline



p-Toluidine

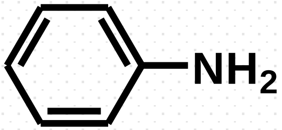


o-Toluidine

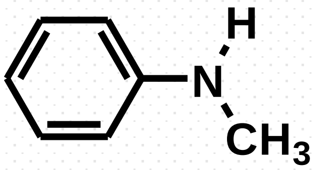


m-Toluidine

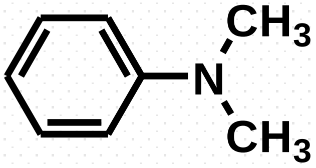
Classification of aromatic amines



1^{ry} amine



2^{ry} amine



3^{ry} amine

N,N-Dimethylamine

Basicity of Amines

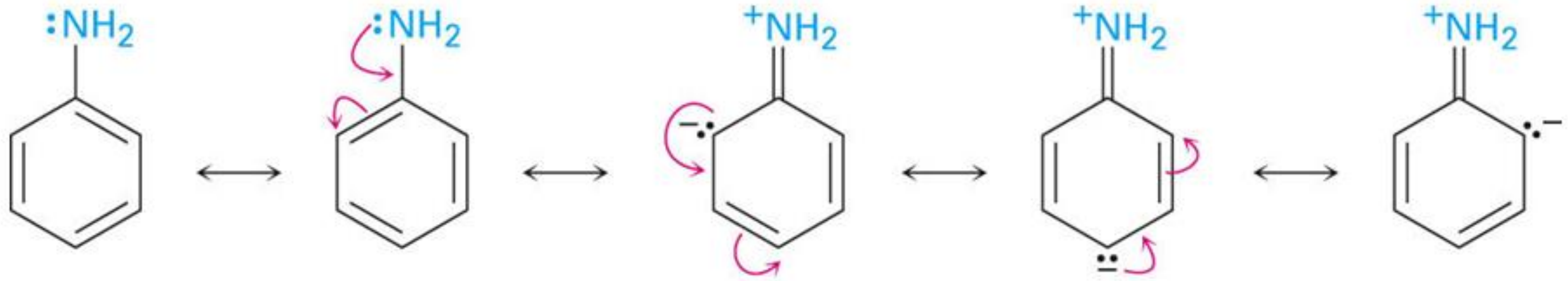
The basicity is reflective of and is expressed as the pK_a's of the conjugate acid. The conjugate base of a weak acid is a strong base:

Higher pK_a = weaker acid = stronger conjugate base

The conjugate base of a strong acid is a weak base

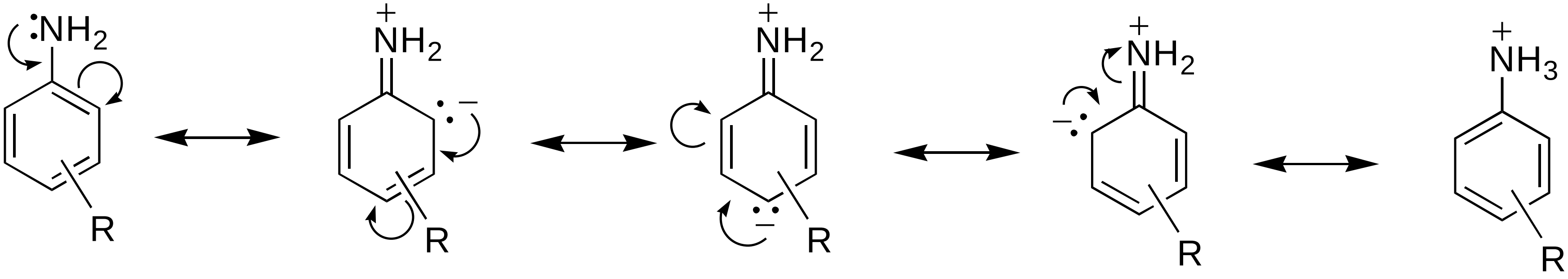
Lower pK_a = stronger acid = weaker conjugate base

- The N lone-pair electrons in aryl amines are delocalized by interaction with the aromatic ring π electron system and are less able to accept H^+ than are alkyl amines.
- Electron withdrawing effect of phenyl group Inductive effect.
- Also sp2 hybridization of carbon on phenol…more electronegative than sp3 hybridized carbon atoms.



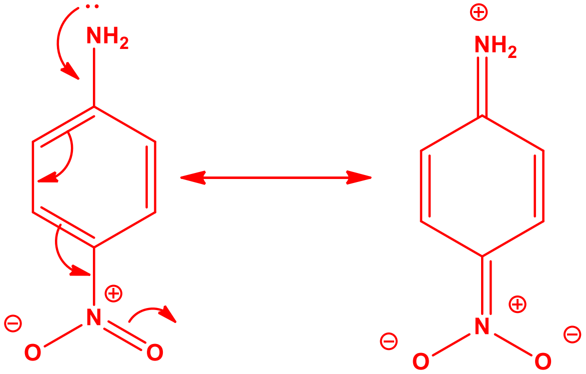
Aryl amines are much less basic than alkyl amines. The lone pair of electrons on the nitrogen of aniline are conjugated to the π-electrons of the aromatic ring and are therefore less available for acid-base chemistry. Protonation disrupts the conjugation.

Substituents can greatly influence the basicity of the aniline. The effect is dependent upon the nature and position of the substituent.



Electron-donating substituents (-CH_3, -OH, -OCH_3) make the substituted aniline more basic than aniline itself (the pK_a of the anilinium ion is higher than 4.6).

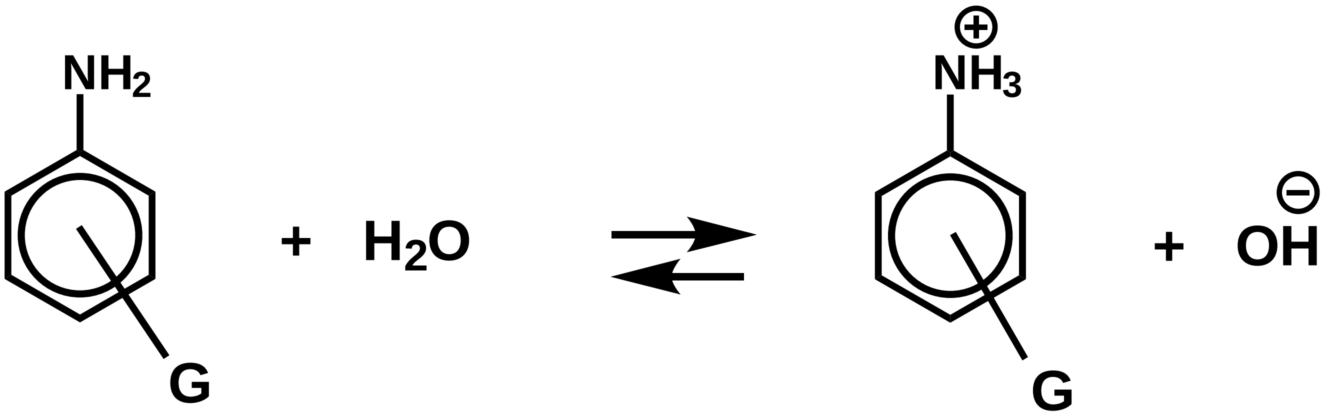
Electron-withdrawing substituents (-Cl, -NO_2) make the substituted aniline less basic than aniline itself (the pKa of the anilinium ion is lower than 4.6).
The reason : withdrawing groups decrease the electronic density for the nitrogen atom by the negative resonance.



Y= -NH_2	pK_a= 6.2
-OCH_3	pK_a= 5.3
-CH_3	pK_a= 5.1
-H	pK_a= 4.6
-Cl	pK_a= 4.0
-CF_3	pK_a= 3.5
-CN	pK_a= 1.7
-NO_2	pK_a= 1.0

less acidic
(more basic)

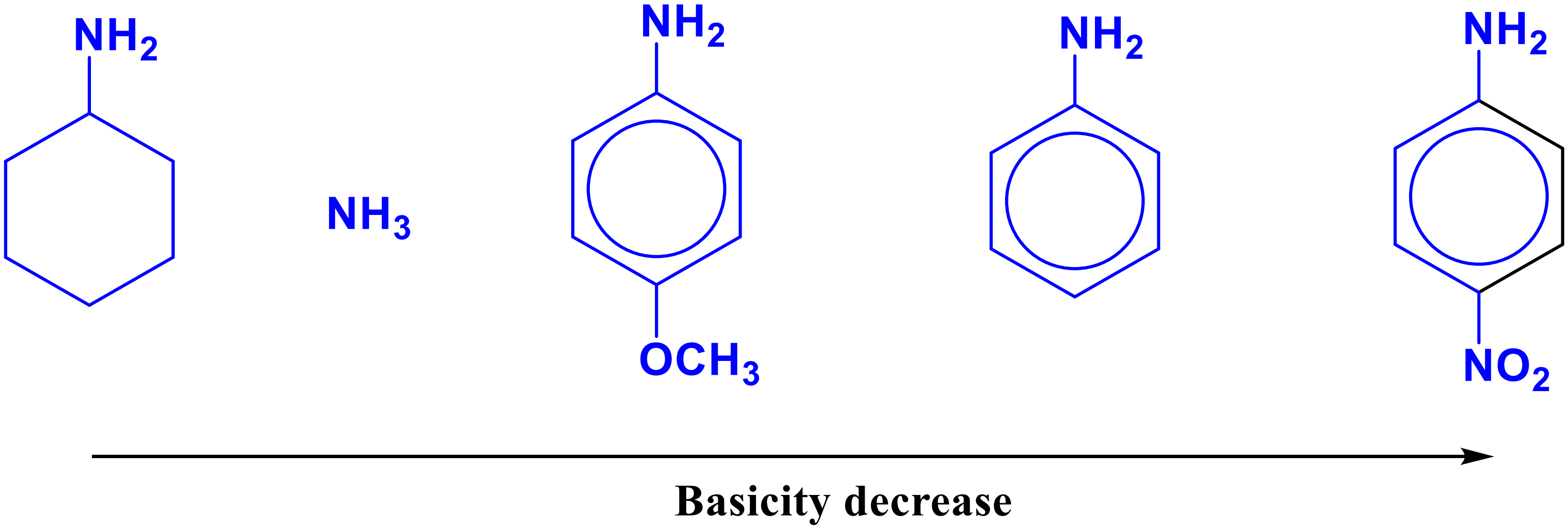
more acidic
(less basic)



Electron donating groups will stabilize the anilinium ion, decreasing the ΔH, shifting the ionization farther to the right and making the compound a stronger base.

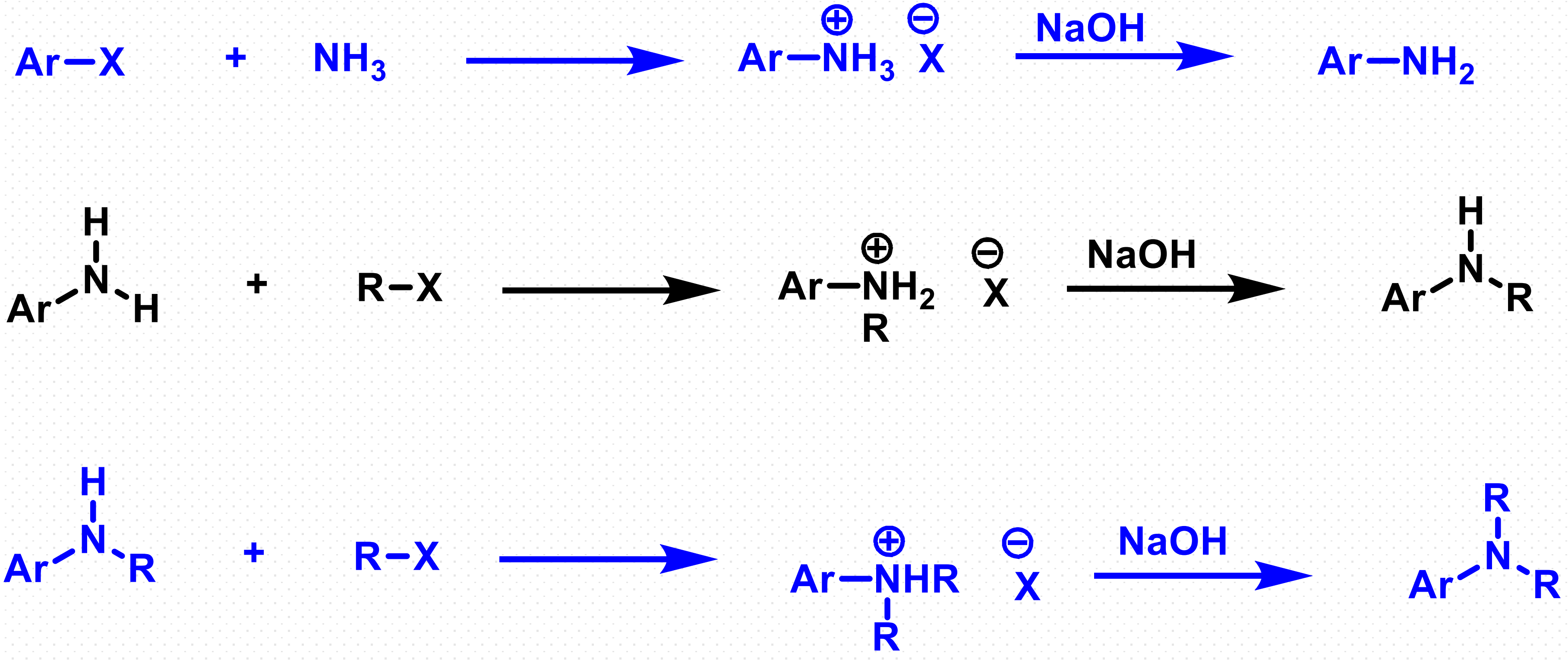
Electron withdrawing groups destabilize the anilinium ion, increasing the ΔH, shifting the ionization towards the reactants, making the compound a weaker base.

Number the following in decreasing order of base strength



Methods of preparation

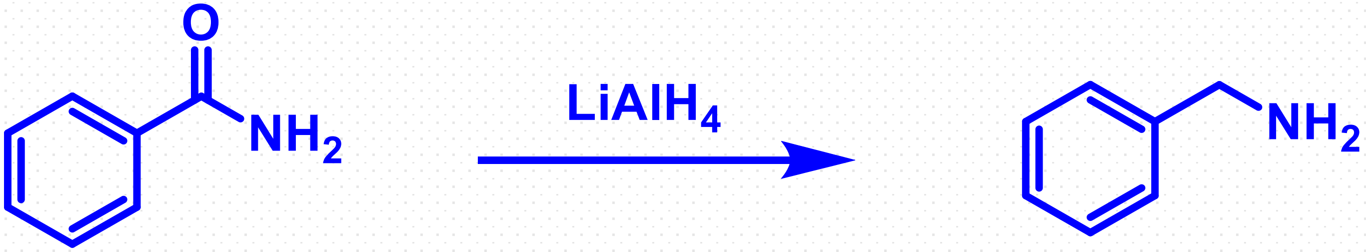
1) Alkylation of ammonia



$$Ar{-}X + NH_3 \longrightarrow Ar{-}\overset{\oplus}{N}H_3\ \overset{\ominus}{X} \xrightarrow{NaOH} Ar{-}NH_2$$

2) Reduction of nitro compounds

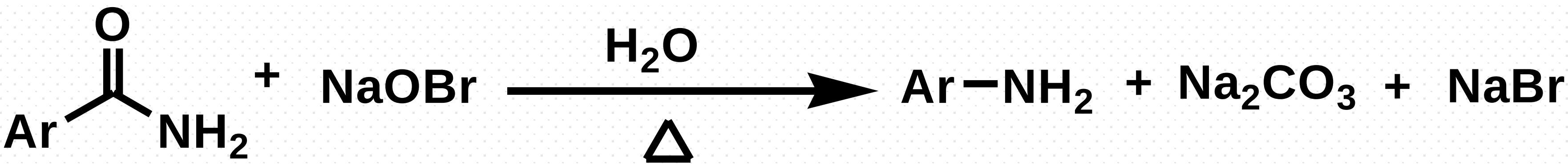
3) Reduction of amides



Benzamide

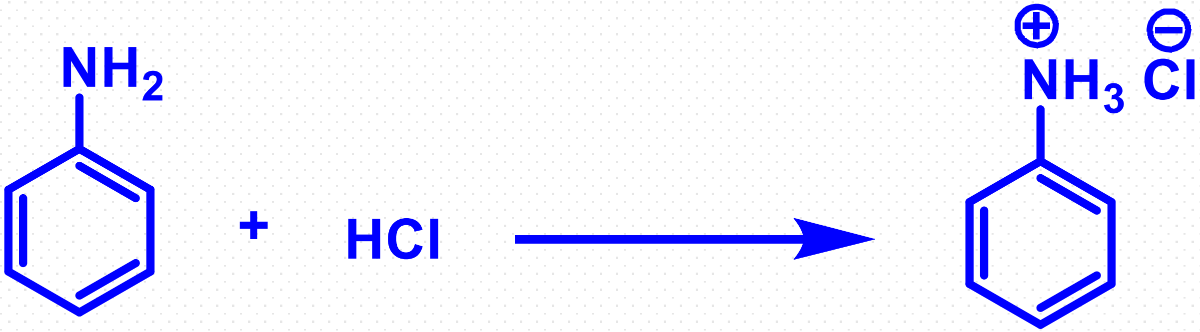
Benzylamine

4) Hoffmann degradation of amides



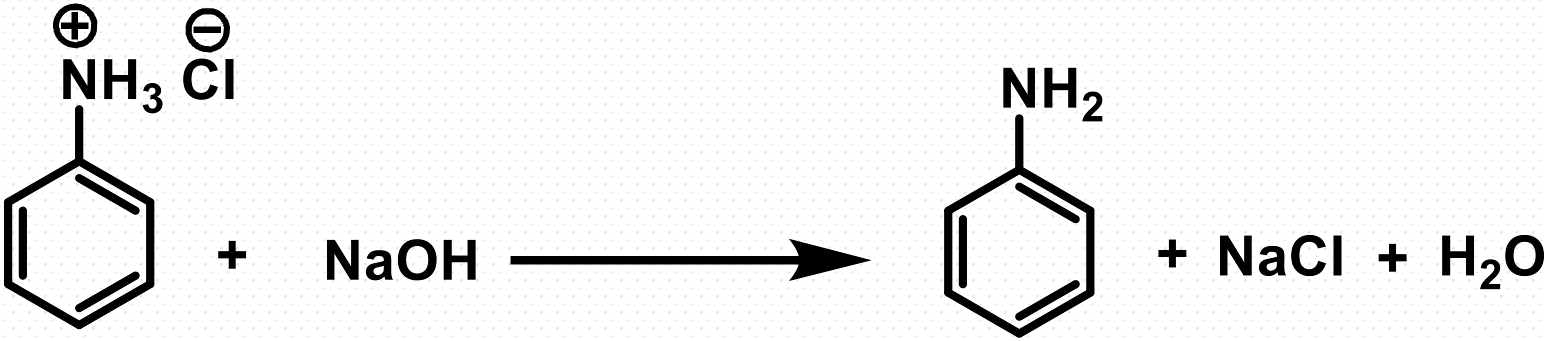
Reactions of amines

1) Salt formation

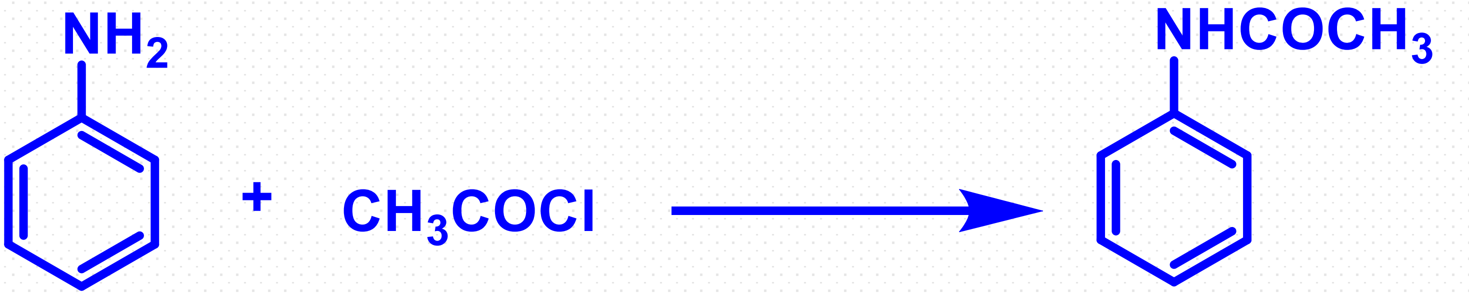


Aniline hydrochloride

Quaternary ammonium salt

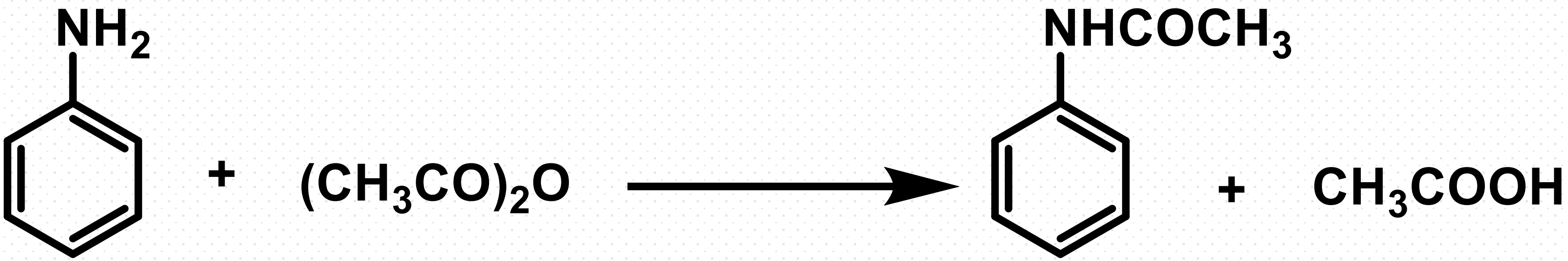


2) Acylation



Acetylchloride

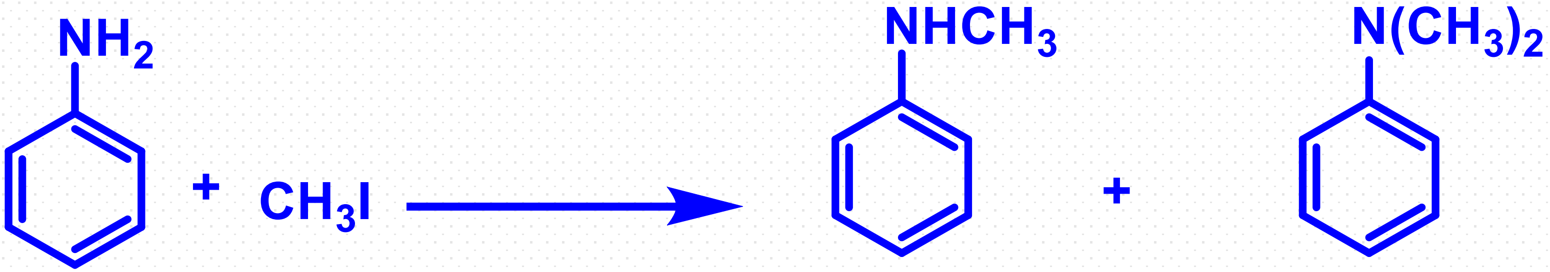
Acetanilide



Acetic anhydride

Acetanilide

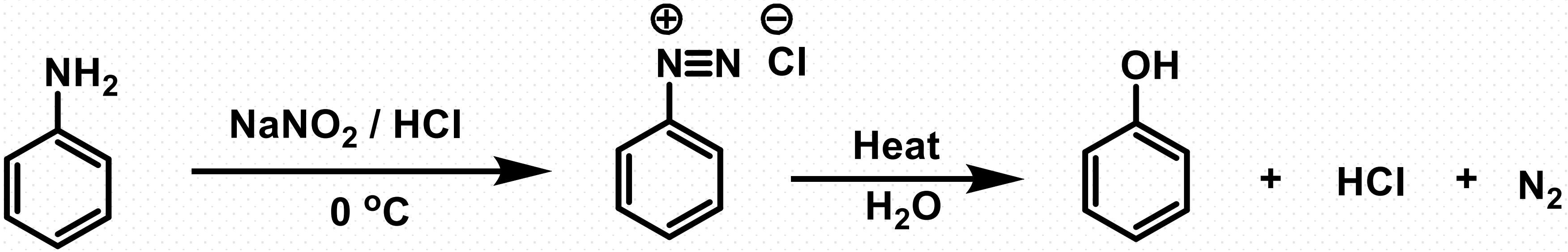
3) Alkylation



Iodomethane *N-Methylaniline* *N,N-Dimethylaniline*

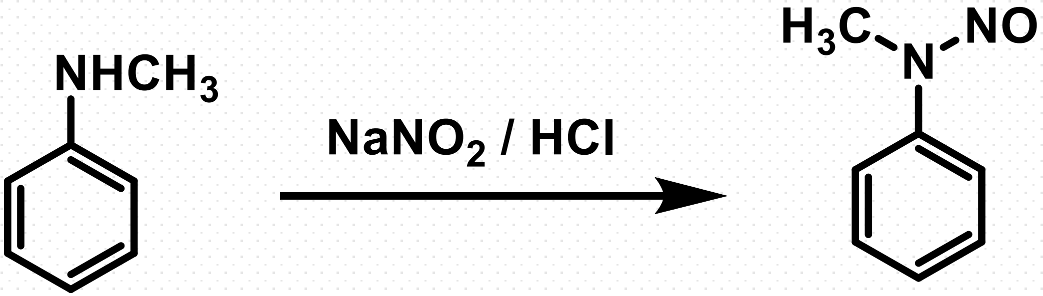
4) Action of nitrous acid

a) primary aromatic amines



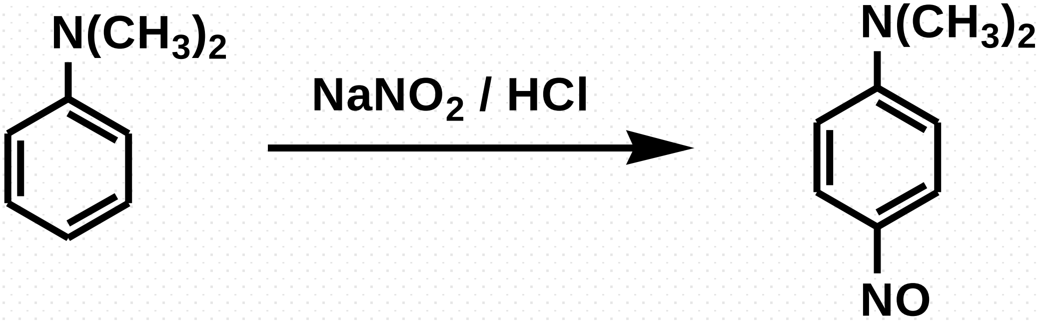
Benzenediazonium chloride

b) secondary aromatic amines



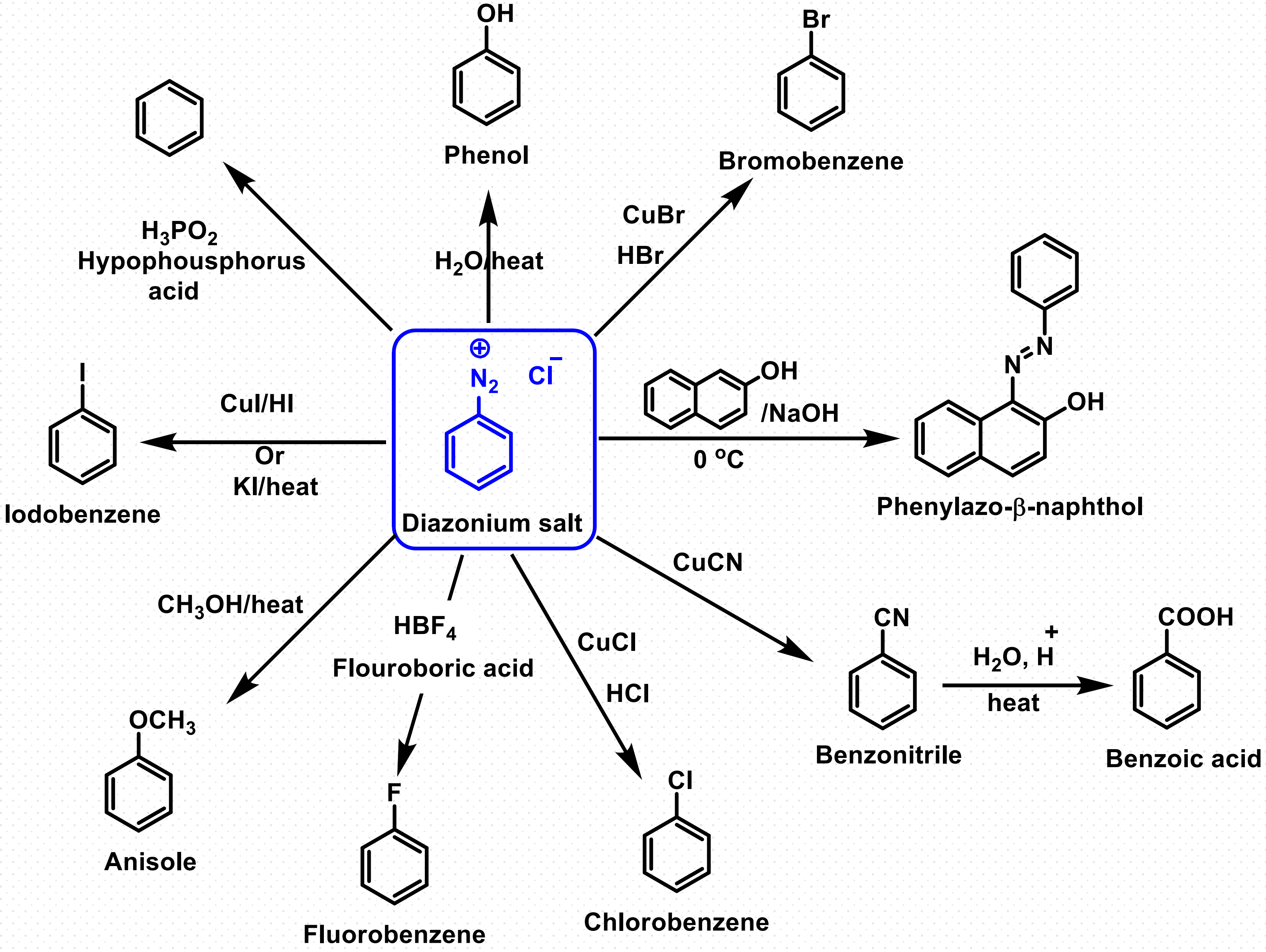
N-Nitrosomethylaniline

c) tertiary aromatic amines

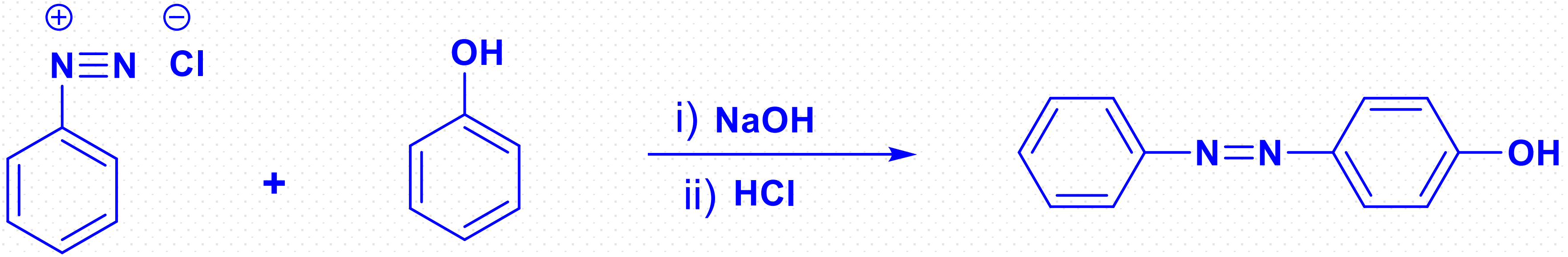


p-Nitroso-N,N-dimethylaniline

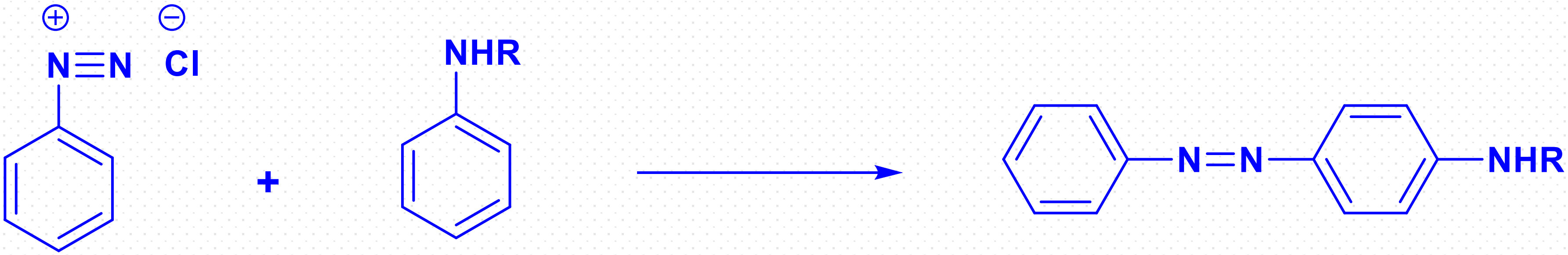
Reactions of diazonium salts



Azo dye formation



Benzene azo phenol



R = CH_3

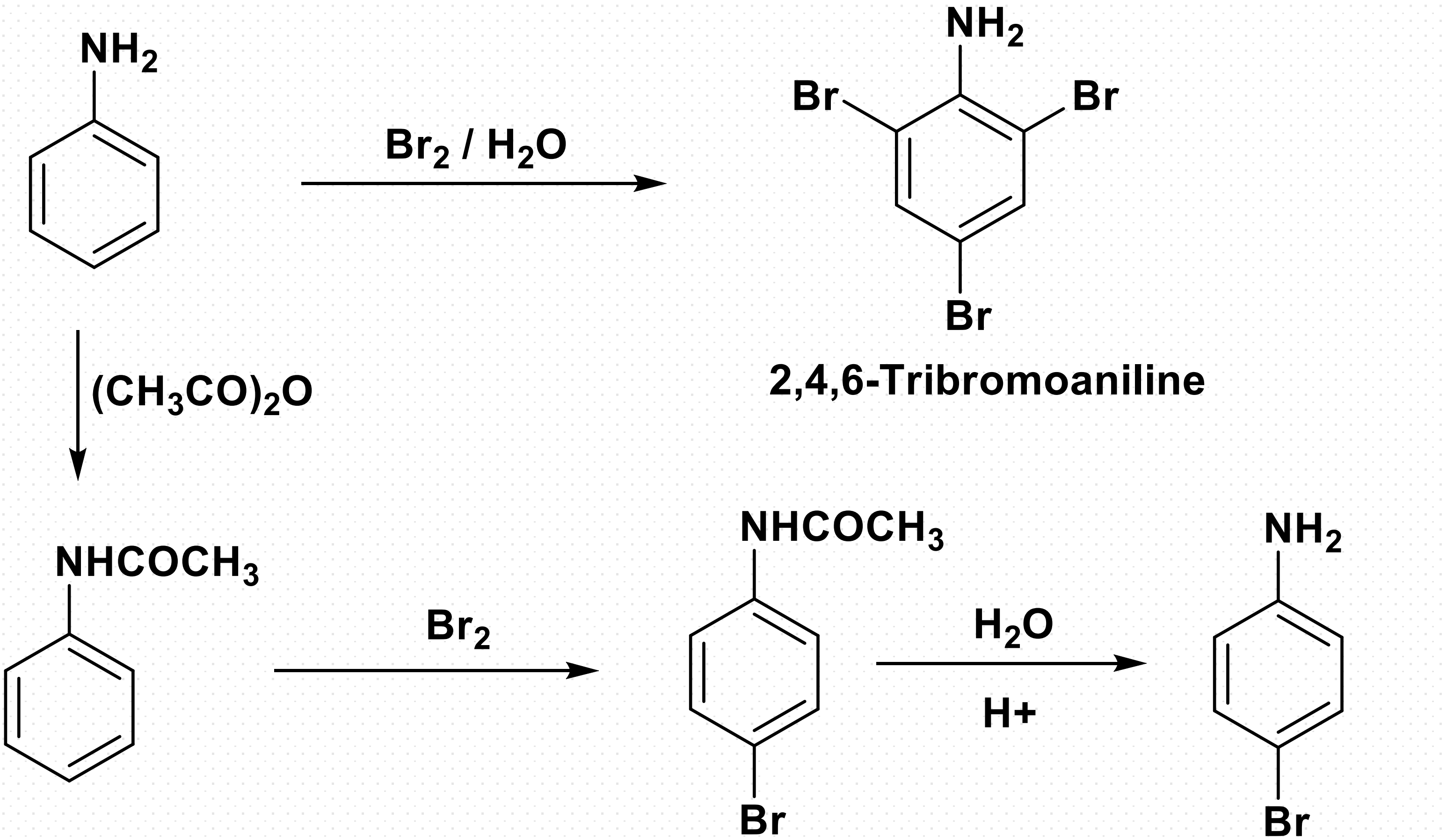
4-N-Methylamino azobenzene

5) Carbylamine (isocyanide) test

Phenylisocyanide

Electrophilic Substitution reactions

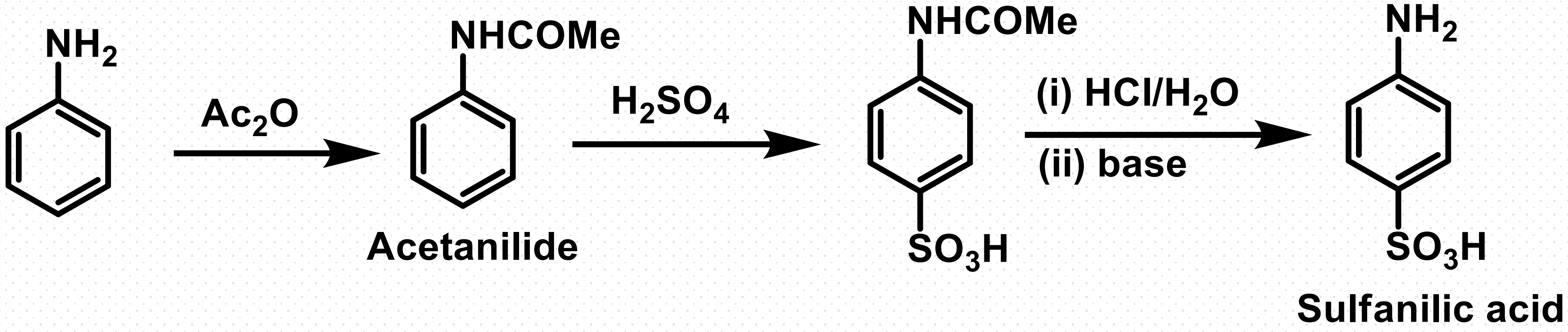
1) Halogenations



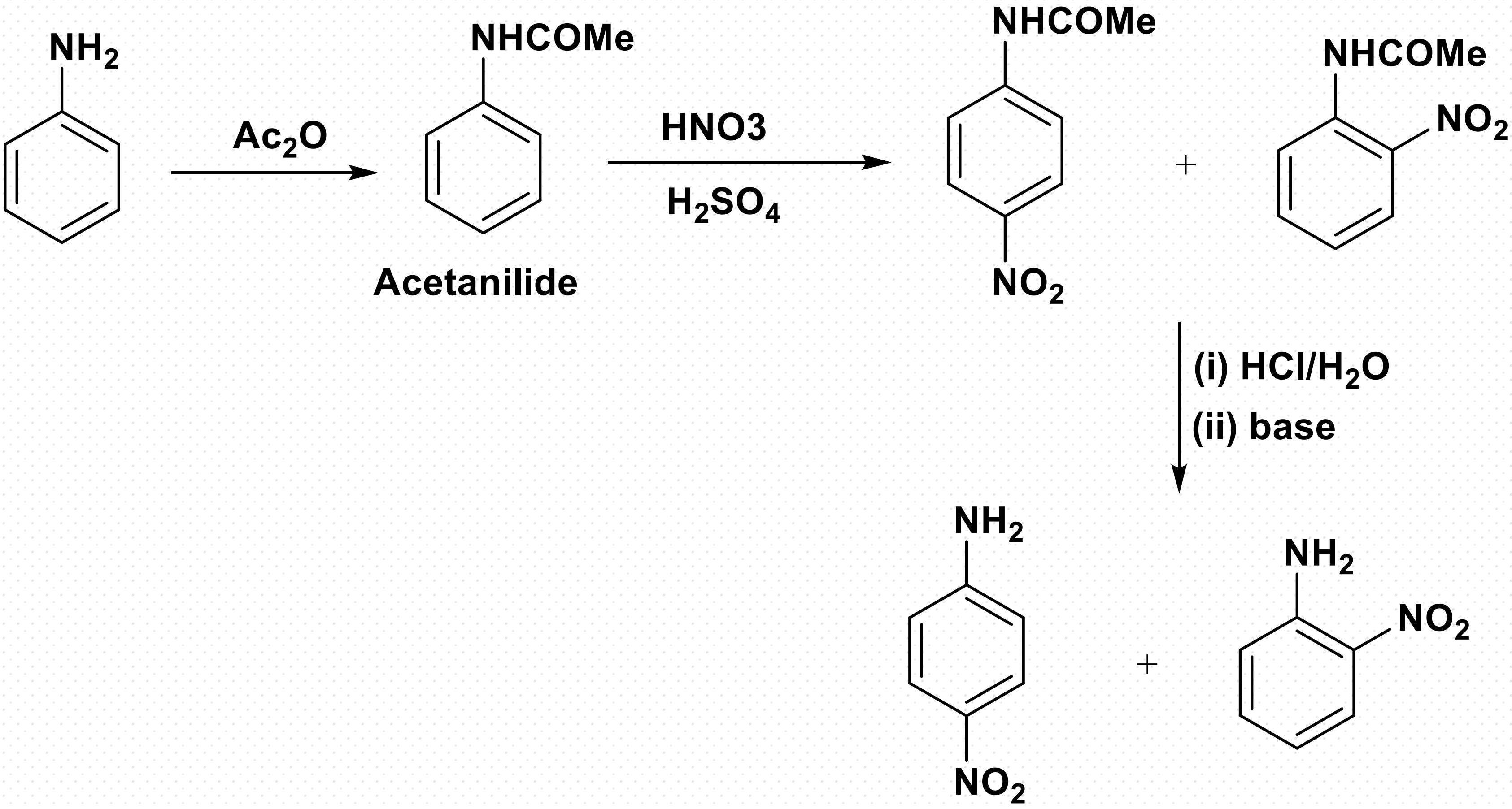
2,4,6-Tribromoaniline

***p*-Bromoaniline**

2) Sulfonation



3) Nitration


NH$_2$
Ac$_2$O
NHCOMe
Acetanilide
HNO3
H$_2$SO$_4$
NHCOMe
NO$_2$
+
NHCOMe
NO$_2$
(i) HCl/H$_2$O
(ii) base
NH$_2$
NO$_2$
+
NH$_2$
NO$_2$

4-Hinsberg test (separation of mixtures of amines)

$$\mathrm{RNH_2} \xrightarrow{\mathrm{C_6H_5SO_2Cl\ /\ 2\ NaOH}} \underset{\textbf{Soluble}}{\mathrm{C_6H_5SO_2\overset{-}{N}R\ \overset{+}{Na}}} \xrightarrow{\mathrm{H^+}} \underset{\textbf{Insoluble}}{\mathrm{C_6H_5SO_2NHR}}$$

$$\mathrm{R_2NH} \xrightarrow{\mathrm{C_6H_5SO_2Cl\ /\ 2\ NaOH}} \underset{\textbf{Insoluble}}{\mathrm{C_6H_5SO_2NR_2}} \xrightarrow{\mathrm{H^+}} \textbf{No reaction}$$

$$\mathrm{R_3N} \xrightarrow{\mathrm{C_6H_5SO_2Cl\ /\ 2\text{-}NaOH}} \textbf{No reaction} \xrightarrow{\mathrm{H^+}} \textbf{No reaction}$$

REFERENCES

1. J. D. Hepworth, D. R. Waring and M. J. Waring. "*Aromatic Chemistry*", RSC 2002, ISBN: 0-85404-662-3.
2. J. McMurry. "*Organic Chemistry*", 9th Edition, Cengage Learning, 2015.