CONCEPT MAP

ORGANIC COMPOUNDS CONTAINING NITROGEN

Amines

$R-NH_2$

Common name: Alkylamines
IUPAC name: Alkanamines

sp^3-C — R — N — Alkyl amine
sp^2-C — Ar — N — Aromatic amine

Classified as : $R-NH_2$ (1°);
$\begin{matrix}R\\R'\end{matrix}>NH$ (2°); $\begin{matrix}R\\R'\\R''\end{matrix}>N$ (3°)
$R_4N^+X^-$ (4°- ammonium salt)

Preparation

- $R-COOH + N_3H \xrightarrow[\text{Schmidt reaction}]{\text{Conc. } H_2SO_4} R-NH_2$
- $R-CN \xrightarrow[\text{Mendius reaction}]{H_2/Ni,\ Na/C_2H_5OH} R-NH_2$
- $R-NO_2 \xrightarrow{Sn/HCl,\ LiAlH_4} R-NH_2$
- Gabriel phthalimide synthesis: $\xrightarrow[H_3O^+,\ \Delta]{+KOH;\ C_6H_5X}$

Chemical Properties

- $R-NH_2 \xrightarrow[\text{Carbylamine reaction}]{CHCl_3+3KOH,\ \Delta} RNC$ (Alkyl isocyanide)
- $R-NH_2 \xrightarrow[\Delta]{R'-CHO} RN=CHR'$ (Schiff's base / Aldimine)

Basic Nature

- Aliphatic amine > NH_3 > aromatic amine
- 3° > 2° > 1° > NH_3 [in gas phase or in non aq. solvent]
- 2° > 1° > 3° > NH_3 [in aq. phase, only $-CH_3$ subs. amine]
- 2° > 3° > 1° > NH_3 [in aq. phase, only $-C_2H_5$ subs. amine]

Special Hofmann Reactions

- **Hofmann's method (Separation of 1°, 2° and 3° amines):**
  Diethyloxalate + 1° – 2° – 3° amines
  - Oxamide, solid (1° amine)
  - Oxamic ester, liquid (2° amine)
  - No reaction (3° amine)
- **Hofmann's ammonolysis (Mix. of amines is formed):** $RX + NH_3 \longrightarrow$ 1° 2° 3° 4° Amines
- **Hofmann's bromamide/degradation (Only 1° amine is formed):**
  $R-CONH_2 + Br_2 + 4KOH \xrightarrow{\Delta} R-NH_2 + 2KBr + K_2CO_3 + 2H_2O$
- **Hofmann's mustard oil reaction (Test for only 1° amine)**
  $R-NH_2 + CS_2 + HgCl_2 \xrightarrow{\Delta} R-N=C=S + HgS + 2HCl$
  Alkyl isothiocyanate

Distinction Tests

- **Liebermann's nitroso test:**
  HONO + 1° + 2° + 3° amines
  - $R-OH + N_2\uparrow + H_2O$ [For 1° amine]
    (Exception - CH_3NH_2 from methyl nitrite or dimethyl ether)
  - $R_2NNO + H_2O$ [For 2° amine]
    N-Nitrosodialkylamine (yellow oily liquid)
  - $[R_3NH]^+NO_2^- \xrightarrow{\Delta} R-OH + R_2NN=O$
    Nitrite salt — Nitrosoamine
    [For 3° amine]
- **Hinsberg's test:**
  $C_6H_5SO_2Cl$ + 1° + 2° + 3° amines
  - Clear solution $\xrightarrow{KOH}$ Soluble salt [For 1° amine]
  - $PPt. \xrightarrow{KOH}$ No reaction. [For 2° amine]
  - No reaction [For 3° amine]

Cyanides

$R-C\equiv N$

Common name: Alkyl cyanides
IUPAC name: Alkane nitriles

Preparation

- $RX + KCN \xrightarrow[\Delta]{\text{aq. alc., } 100\,^\circ C} RCN$
- $R-CONH_2 \xrightarrow[\Delta]{P_2O_5} RCN$
- $R-NH_2 \xrightarrow[300\,^\circ C]{Cu/Ni} RCN$

Chemical Properties

RCN
- $\xrightarrow[SnCl_2/HCl]{+2[H]} RCHO$ (Stephen's reaction)
- $\xrightarrow{RMgX} RCOR'$
- $\xrightarrow[\text{alk. } H_2O_2]{H_2O} RCOOH$

Isocyanides

$R-N\rightarrow C$

Common name: Alkyl isocyanides
IUPAC name: Alkyl carbylamines

Preparation

- $RX + AgCN \xrightarrow[\Delta]{C_2H_5OH} RNC$
- $RCONHR \xrightarrow[\text{Pyridine}]{POCl_3} RNC$

Chemical Properties

RNC
- $\xrightarrow{H_2O/H^+} RNH_2$
- $\xrightarrow[Na/C_2H_5OH]{+4[H]} RNHCH_3$
- $\xrightarrow[250\,^\circ C]{\Delta} RCN$

Nitro

$R-NO_2$

IUPAC name: Nitroalkanes

Preparation

- $R-X + AgNO_2 \xrightarrow{\Delta} R-NO_2$
- $R(Cl)COOH \xrightarrow[-NaCl/\Delta]{NaNO_2} R-NO_2$

Chemical Properties

- $\xrightarrow[\text{explosive}]{\Delta} 1/2N_2 + CO_2 + 3/2H_2$
- $\xrightarrow[Sn/HCl\ (acidic)]{+6[H]} RNH_2$
- $\xrightarrow[Zn + NH_4Cl\ (neutral)]{+4[H]} R-NHOH$
- $\xrightarrow[Aq.\ TiCl_3]{} R-CHO$

Aromatic Compounds

Diazonium Salt

$C_6H_5N_2^+Cl^-$
- $\xrightarrow[\Delta]{CuCl/HCl} C_6H_5Cl$ [Sandmeyer reaction]
- $\xrightarrow{Cu/HCl} C_6H_5Cl$ [Gattermann reaction]
- $\xrightarrow[NaOH,\ \Delta]{C_6H_6} C_6H_5-C_6H_5$ [Gomberg reaction]
- $\xrightarrow{2\text{-naphthol}} C_6H_5N=NC_6H_4OH$ [Coupling reaction]
- $\xrightarrow{H_2O/H^+} C_6H_5OH$
- $\xrightarrow{HBF_4/\Delta} C_6H_5F$

Aniline

Preparation

- $C_6H_6 - Cl - NH_2 \xrightarrow[\Delta]{\text{Anhy. } AlCl_3} C_6H_5NH_2$
- $C_6H_5COOH + N_3H \xrightarrow[\text{Schmidt reaction}]{\text{Conc. } H_2SO_4} C_6H_5NH_2$
- $C_6H_5OH + NH_3 \xrightarrow[300\,^\circ C]{\text{Anhy. } ZnCl_2} C_6H_5NH_2$

Chemical Properties

- $\xrightarrow[0-5\,^\circ C]{HCl} C_6H_5NH_3^+Cl^-$
- $\xrightarrow{[O]/\text{acidified } KMnO_4}$ Aniline black
- $\xrightarrow{[O]/\text{alkaline } KMnO_4}$ Azobenzene
- $\xrightarrow{[O]/\text{neutra. } KMnO_4}$ Azobenzene and nitrobenzene

Nitrobenzene

$C_6H_5NO_2$

- $\xrightarrow{3\,H_2}$ $H_2NC_6H_4OH$ (p-Amino phenol) $\xleftarrow{\text{Isomeric change}}$
- $\xrightarrow{2[H]}$ C_6H_5NO (Nitrosobenzene) $\xrightarrow{2[H]}$ C_6H_5NHOH (Phenylhydroxyl amine) $\xrightarrow[Sn + HCl]{\text{acidic}}$ $C_6H_5NH_2$ (Aniline)

Na_3AsO_3 + NaOH — in alkaline medium

C_6H_5N (Azoxybenzene) $\xrightarrow{O}$ $\xrightarrow[Zn + NaOH]{}$ C_6H_5N (Azobenzene) $\xrightarrow[Zn + NaOH]{}$ C_6H_5NH (Hydrazobenzene)