CONCEPT MAP

ORGANIC COMPOUNDS CONTAINING NITROGEN

Amines

N → sp^3, classified as 1°, 2°, 3° depending upon the no. of H atoms replaced by alkyl or aryl groups in NH_3.
IUPAC name : alkanamines or arylamines.

Properties

Physical

- Lower aliphatic → soluble in H_2O (H-bonding)
  Solubility ∝ 1/molarmass
  Aromatic amines → insoluble in H_2O
- B.P. : 1° > 2° > 3°
  B.P. ∝ intermolecular H-bonding
  Acids > alcohols > amines > hydrocarbons

Chemical

- **Basicity:** 2° > 3° > 1°
  Ethylamine > NH_3 > aniline
- EDG → increases basicity
  EWG → decreases basicity
- With alkyl halides → alkylation
- 1° and 2° with acid chlorides, anhydrides, esters → nucleophilic substitution
- 1° amines on heating with $CHCl_3$ and KOH → form isocyanides or carbylamines → **Carbylamine reaction**
  1° aliphatic amines $\xrightarrow{HNO_2}$ alcohol
  Aromatic amines $\xrightarrow{HNO_2}$ diazonium salts
- 1° and 2° + $C_6H_5SO_2Cl$ (Hinsberg's reagent) → sulphonamides
- Electrophilic substitution : *o*- and *p*-substituting
- 1° and 2° amines + $R - MgX$ →

Diazonium Salts

$RN_2^+X^-$

Conversion of 1° aromatic amines into diazonium salts → diazotisation.

Chemical reactions

- **Displacement of N :**

$$ArN_2^+X^- \xrightarrow{CuCl/HCl} ArCl + N_2$$
$$ArN_2^+X^- \xrightarrow{CuBr/HBr} ArBr + N_2$$
$$ArN_2^+X^- \xrightarrow{CuCN/KCN} ArCN + N_2$$

Sandmeyer reaction

$$ArN_2^+X^- \xrightarrow{Cu/HCl} ArCl \qquad ArN_2^+X^- \xrightarrow{Cu/HBr} ArBr$$

Gatterman reaction

$$ArN_2^+Cl^- \xrightarrow{KI} ArI$$
$$ArN_2^+Cl^- \xrightarrow[\Delta]{HBF_4} Ar-F$$
$$ArN_2^+Cl^- \xrightarrow{H_2O} ArOH$$
$$ArN_2^+Cl^- \xrightarrow{H_3PO_2 + H_2O} ArH$$
$$ArN_2^+Cl^- \xrightarrow{CH_3CH_2OH} ArH$$

Deamination

$$ArN_2^+Cl^- \xrightarrow{HBF_4} ArN_2^+BF_4^- \xrightarrow[Cu,\ \Delta]{NaNO_2} ArNO_2$$

- **Retention of diazogroup :**
  Coupling reactions : Form coloured azo compounds (Ar–N=N–Ar) with highly reactive – phenols and amines.