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Subject: Chemistry
Weightage: Regular
Title: Nitrogen-Containing Organic Compound

Organic Compounds Containing Nitrogen

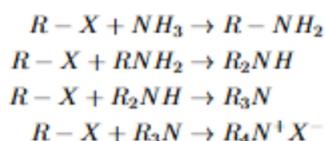
Amines

Amines are derivatives of ammonia where one or more hydrogen atoms are replaced by alkyl or aryl groups.

Preparation of Amines

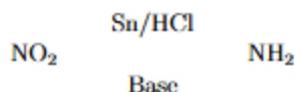
1. Alkylation of Ammonia

Alkyl halides react with ammonia via S_N2 mechanism:

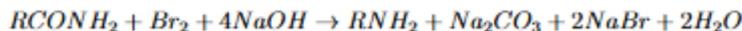


2. Reduction of Nitro Compounds

Nitro groups can be reduced to amines:



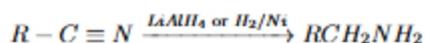
3. Hofmann Bromamide Degradation



4. Gabriel Synthesis

Phthalimide reacts with alkyl halides followed by hydrolysis to give primary amines.

5. Reduction of Nitriles



6. Reduction of Isonitriles



7. Reduction of Amides



8. Reductive Amination

Aldehydes and ketones form imines with ammonia which are then reduced to amines.

Physical Properties of Amines

- Gases (lower aliphatic), liquids or solids (higher ones and aromatic amines)
- Soluble in water (small amines), solubility decreases with size
- Higher boiling points than hydrocarbons; lower than alcohols
- Fishy smell (lower amines)

Chemical Properties of Amines

1. Basic Character



Order of basic strength:

- Gas phase: tertiary > secondary > primary > NH_3
- Aqueous: secondary > primary > tertiary > NH_3 (for CH_3)
secondary > tertiary > primary > NH_3 (for C_2H_5)
- Aryl amines | aliphatic due to resonance

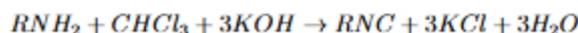
2. Alkylation



3. Acylation

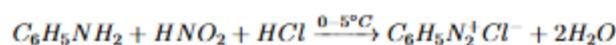


4. Carbylamine Test



5. Reaction with Nitrous Acid

- Primary aliphatic: unstable diazonium salts \rightarrow alcohols + N_2
- Secondary: yellow oily N-nitrosoamines
- Tertiary: ammonium nitrites
- Aromatic: stable diazonium salts



6. Hinsberg Test

- Primary: soluble sulphonamide
- Secondary: insoluble
- Tertiary: no reaction

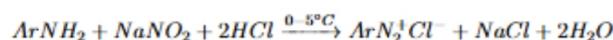
7. Electrophilic Substitution

- Bromination: gives 2,4,6-tribromoaniline
- Nitration: via acetylated protection
- Sulphonation: forms sulfanilic acid

Diazonium Salts

Stable at 0-5°C

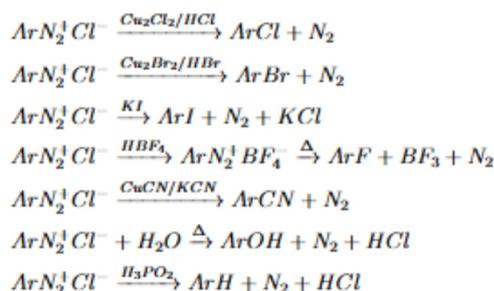
Preparation



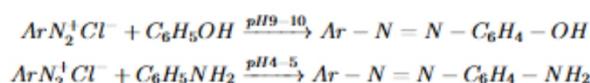
Properties

- Crystalline solids
- Soluble in water
- Unstable at room temp

1. Displacement Reactions

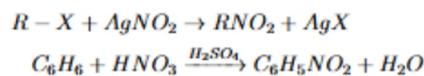


2. Coupling Reactions



Nitro Compounds

Preparation



Properties

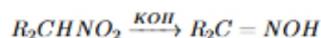
- Nitroalkanes: colorless liquids
- Nitroarenes: pale yellow solids/liquids
- Sparingly water-soluble
- High boiling points

Reactions

- **Reduction:**

- Neutral: $RNO_2 \rightarrow R-NHOH$
- Acidic: $RNO_2 \rightarrow RNH_2$
- Basic: forms azoxy, azo, etc.

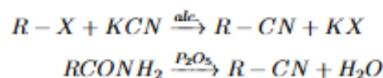
- **Hydrolysis:**



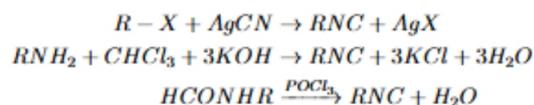
- **With HNO_2 :** gives nitrolic acids (primary), pseudo nitroles (secondary), no reaction (tertiary)

Cyanides and Isocyanides

Preparation of Alkyl Cyanides



Preparation of Alkyl Isocyanides



Properties of Isocyanides

- Colorless, foul-smelling liquids
- Higher boiling than cyanides
- Water-insoluble
- Highly toxic

Reactions of Isocyanides

- **Hydrolysis:** $RNC \rightarrow RNH_2 + HCOOH$
- **Reduction:** $RNC \rightarrow RNHCH_3$