New Reactions

1. Acidity of Amines and Amide Formation (Section 21-4)

$$RNH_2 + H_2O \overset{K}{\rightleftharpoons} R\bar{N}H + H_3O^+ \qquad K_a \approx 10^{-35}$$

$$R_2NH + CH_3CH_2CH_2CH_2Li \rightleftharpoons \underset{\text{Lithium dialkylamide}}{R_2N^-Li^+} + CH_3CH_2CH_2CH_3$$

$$2\,NH_3 + 2\,Na \xrightarrow{\text{Catalytic } Fe^{3+}} 2\,NaNH_2 + H_2$$

2. Basicity of Amines (Section 21-4)

$$RNH_2 + H_2O \rightleftharpoons R\overset{+}{N}H_3 + HO^-$$

$$R\overset{+}{N}H_3 + H_2O \overset{K}{\rightleftharpoons} RNH_2 + H_3O^+ \qquad K_a \approx 10^{-10}$$

Salt formation

$$RNH_2 + HCl \longrightarrow \underset{\text{Alkylammonium chloride}}{R\overset{+}{N}H_3\ Cl^-}$$

General for primary, secondary, and tertiary amines

Preparation of Amines

3. Amines by Alkylation (Section 21-5)

$$R\ddot{N}H_2 + R'X \longrightarrow R\overset{R'}{\overset{|}{\overset{+}{N}}}H_2\ X^-$$

General for primary, secondary, and tertiary amines

Drawback: multiple alkylation

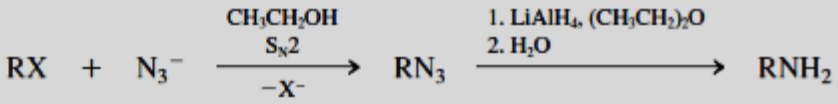
$$R\overset{R'}{\overset{|}{\overset{+}{N}}}H_2\ X^- + R'X \longrightarrow \longrightarrow \longrightarrow R\overset{+}{N}R'_3\ X^-$$

4. Primary Amines from Nitriles (Section 21-5)

$$RX + {}^-CN \xrightarrow[-X^-]{\overset{\text{DMSO}}{S_N2}} RCN \xrightarrow{LiAlH_4 \text{ or } H_2,\ \text{catalyst}} RCH_2NH_2$$

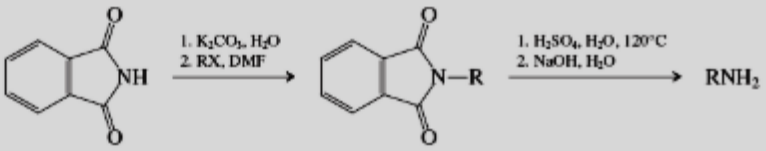
R limited to methyl, primary, and secondary alkyl groups

5. Primary Amines from Azides (Section 21-5)



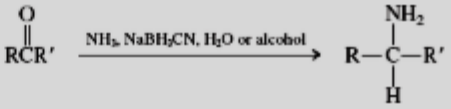
R limited to methyl, primary, and secondary alkyl groups

6. Primary Amines by Gabriel Synthesis (Section 21-5)

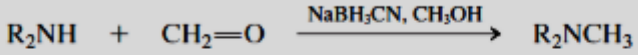


R limited to methyl, primary, and secondary alkyl groups

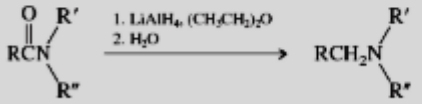
7. Amines by Reductive Amination (Section 21-6)



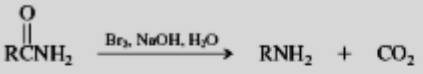
Reductive methylation with formaldehyde



8. Amines from Carboxylic Amides (Section 21-7)

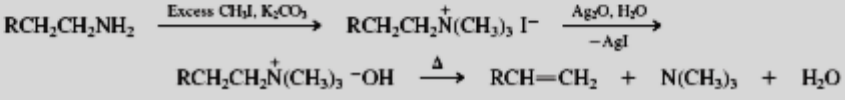


9. Hofmann Rearrangement (Section 21-7)

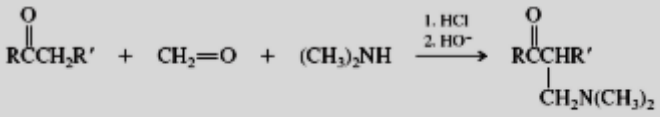


Reactions of Amines

10. Hofmann Elimination (Section 21-8)

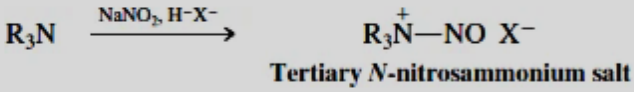


11. Mannich Reaction (Section 21-9)



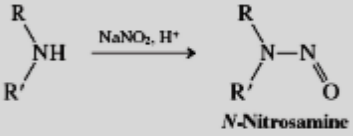
12. Nitrosation of Amines (Section 21-10)

Tertiary amines



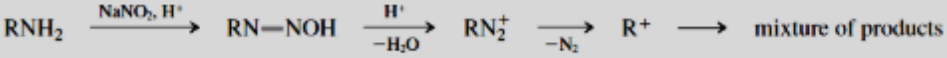
Tertiary *N*-nitrosammonium salt

Secondary amines

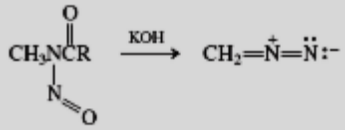


***N*-Nitrosamine**

Primary amines



13. Diazomethane (Section 21-10)



Esterification with diazomethane