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Chapter 22 Summary (Klein): Amines

I. Introduction & Nomenclature: alkanamine or alkyl amine, aniline (22.2) **SkillBuilder 22.1**

II. Properties of Amines (22.3)

A) RNH_2 has lower b.p. than ROH

B) RNH_2 is better Nu./base than ROH

i) alkyl vs. aryl amine basicity; pK_a 's of amine conjugate acids

ii) salts of amines (solubility, medicinal applications, crack cocaine)

III. Reactions of Amines

A) as Nu: ($\text{S}_{\text{N}}2$ with RX makes amine; reaction with RCOCl makes amide)

B) Nitrosation (22.10, 22.11), reaction with HONO ($\text{NaNO}_2 + \text{HA}$)

i) gives diazonium salts (ArN_2^+), useful for synthesis of benzene derivatives

C) Hofmann elimination (22.9) **SkillBuilder 22.5**

i) make amine good LG (excess $\text{CH}_3\text{I} \rightarrow$ quaternary salt)

ii) E2 reaction (Ag_2O , H_2O , Δ)

iii) least substituted alkene formed as major product (opposite of Zaitsev)

D) reaction with aldehydes/ketones to give imines and enamines (19.6)

IV. Preparation of Amines (synthesis) **SkillBuilder 22.4**

A) $\text{RX} \rightarrow \text{RNH}_2$ (22.5) **SkillBuilder 22.2**

i) Gabriel synthesis (phthalimide anion Nu:, then hydrolysis)

ii) azide Nu:, then reduction (NaN_3 , then H_2/cat or LiAlH_4)

iii) nitrite Nu:, then reduction (NaNO_2 , then H_2/cat or Sn/HCl)

B) $\text{RX} \rightarrow \text{RCH}_2\text{NH}_2$ (22.4)

i) cyanide Nu:, then reduction (NaCN , then H_2/cat or LiAlH_4)

C) ketone/aldehyde $\rightarrow$ amine (22.6) **SkillBuilder 22.3**

i) via reduction of imine (H_2/cat or LiAlH_4)

ii) *in situ* formation of imine: "reductive amination" of carbonyl

D) acid chloride $\rightarrow$ amine (22.4)

i) via reduction of amide (LiAlH_4)

V. Biologically interesting amines (22.1):

