

CHEM 20482 - Basic Organic Chemistry - Chapter 22 Review Amines

Basicity

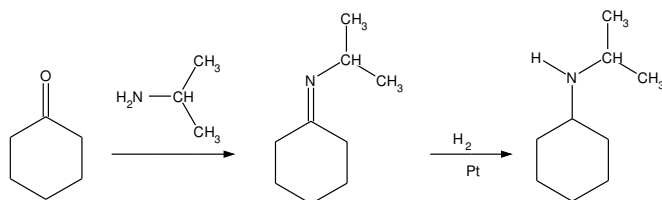
Alkyl amines ($pK_a \sim 9-11$) *more basic than* sp^2 hybridized amines ($pK_a \sim 5-6$) or aryl amines ($pK_a \sim 4-5$)

(See p. 917 of Carey for resonance forms of aniline)

Amine Synthesis

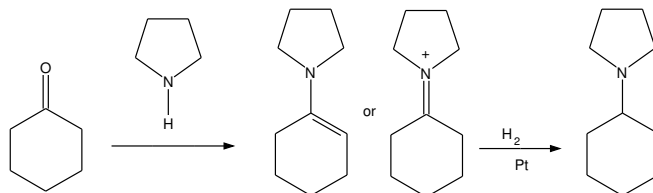
- $R-C\equiv N \xrightarrow[2) H_2O]{1) LiAlH_4} \text{ or } \xrightarrow[Pt]{H_2} R-CH_2-NH_2$
- $R-X + N_3^- \rightarrow R-N=N=N \xrightarrow[2) H_2O]{1) LiAlH_4} \text{ or } \xrightarrow[Pt]{H_2} RNH_2$
- benzene $\xrightarrow[H_2SO_4]{HNO_3} C_6H_5-NO_2 \xrightarrow[2) OH^-]{1) Fe \text{ or } Sn, HCl} \text{ or } \xrightarrow[Pt]{H_2} C_6H_5-NH_2$
- epoxide $\xrightarrow[H_2O]{NH_3} \beta\text{-amino alcohol}$
- $RNH_2 + \text{ketone} \rightarrow \text{imine} \xrightarrow[\text{catalyst}]{H_2} 2^\circ \text{ amine}$

Ex.



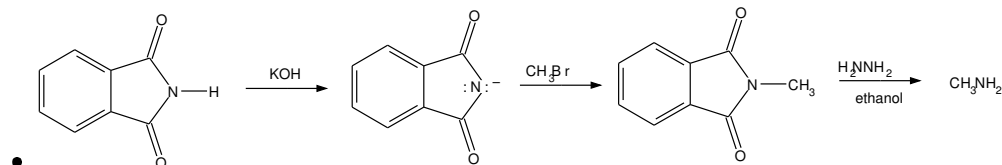
- $RR'NH + \text{ketone} \rightarrow \text{enamine (?) } \xrightarrow[\text{catalyst}]{H_2} 3^\circ \text{ amine}$

Ex.

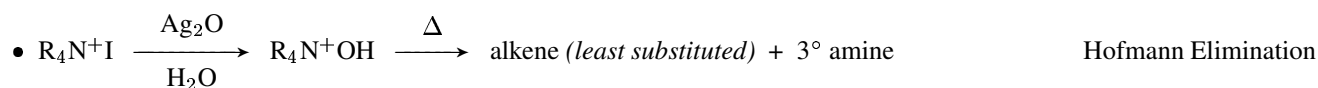
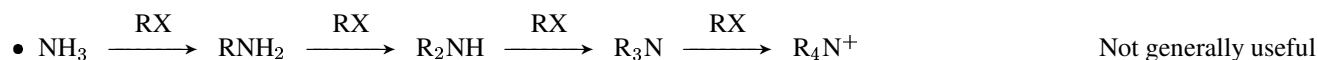


- $RCH_2COOH \xrightarrow[PCl_3]{Br_2} RCH(Br)COOH \xrightarrow{NH_3} \alpha\text{-amino acid}$

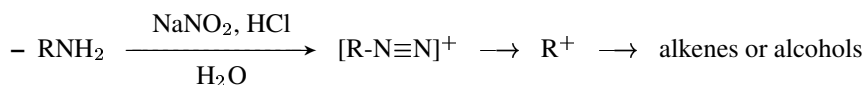
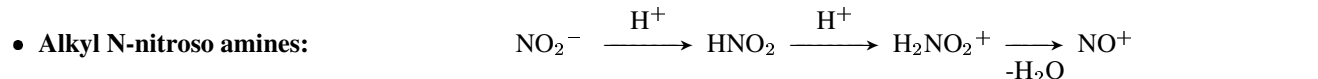
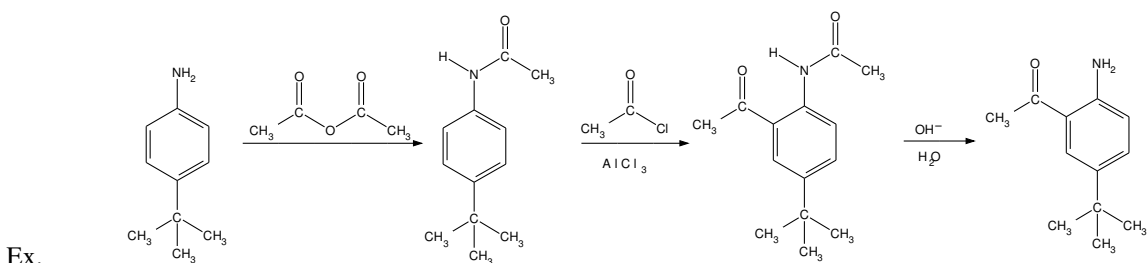
- Acid chloride, anhydride, ester, or acid + 1° or 2° amine \rightarrow amide $\xrightarrow[2) H_2O]{1) LiAlH_4} 1^\circ, 2^\circ, \text{ or } 3^\circ \text{ amine}$



Reactions



- **Aryl substitutions:** NH_2 group is a strongly activating, ortho/para director. Acylation makes this group less activating, and is often required for electrophilic substitution reactions. The acyl group can be removed by hydrolysis with aqueous base (or acid followed by base).



- **Aryl Diazonium Salts** - Intermediate for a number of aromatic substitution reactions

