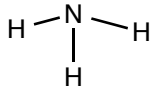
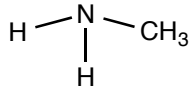
Chapter 23: Amines

[Chapter 23 Sections: 23.1-23.6, 23.11]

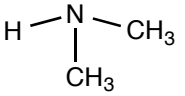
Nomenclature and Classification of Amines



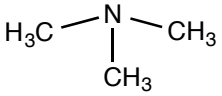
ammonia



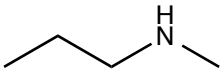
methyl amine
1°

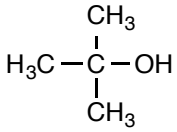


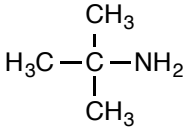
dimethyl amine
2°



trimethyl amine
3°



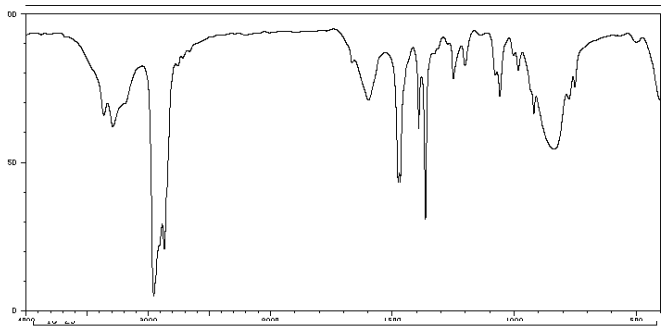


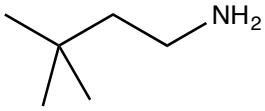


- *simple amines are named by alphabetically placing alkyl substituents before the "amine" suffix*
- *1°, 2° and 3° have a different meaning for amines than other organic compounds, referring NOT to the type of carbon to which the N is attached but to the number of alkyl substituents on the nitrogen*

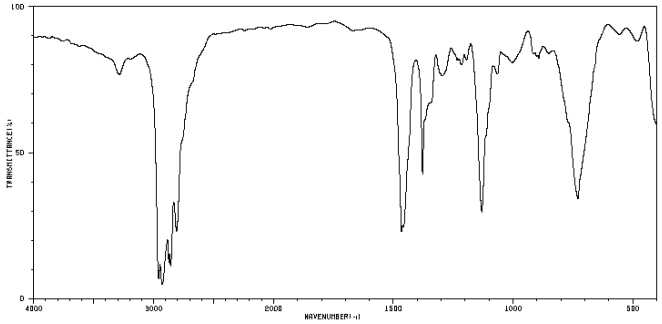
Problems: 1

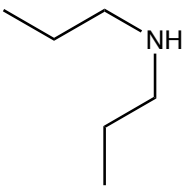
Identification of Amine Class via IR Spectroscopy



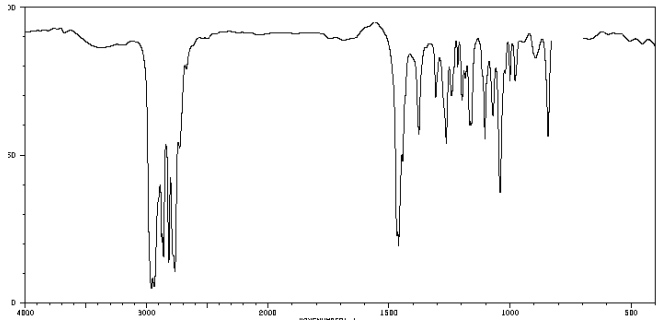


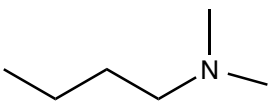
- *1° amines typically show two NH stretches in the 3,500 cm^{-1} region*





- *2° amines typically show one NH stretch in the 3,500 cm^{-1} region*

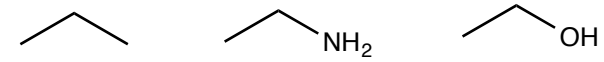




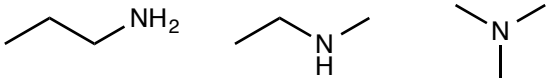
- *3° amines show no NH stretch in the 3,500 cm^{-1} region*

Properties of Amines

boiling points



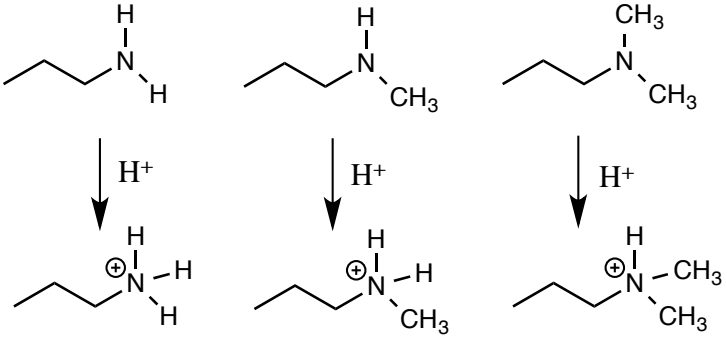
B.P.



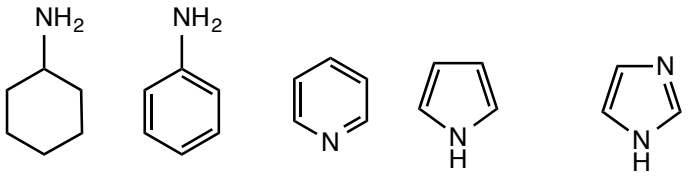
- *amines are polar compounds*
- *1° and 2° amines are capable of hydrogen bonding*
- *the boiling points of isomeric amines (same molecular weight) generally is in the order 1° > 2° > 3° due to decreasing hydrogen bonding effects*

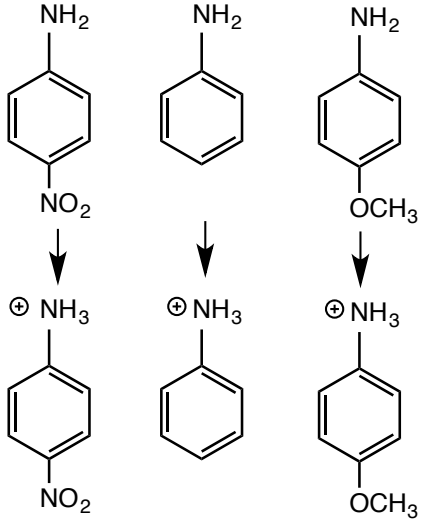
B.P.

basicity



- *basicity is determined by the ability of a nitrogen atom to donate its pair of electrons to the proton*
- *1°, 2° and 3° amines can all act as bases since they all have lone pairs available for forming bonds to a H^+*



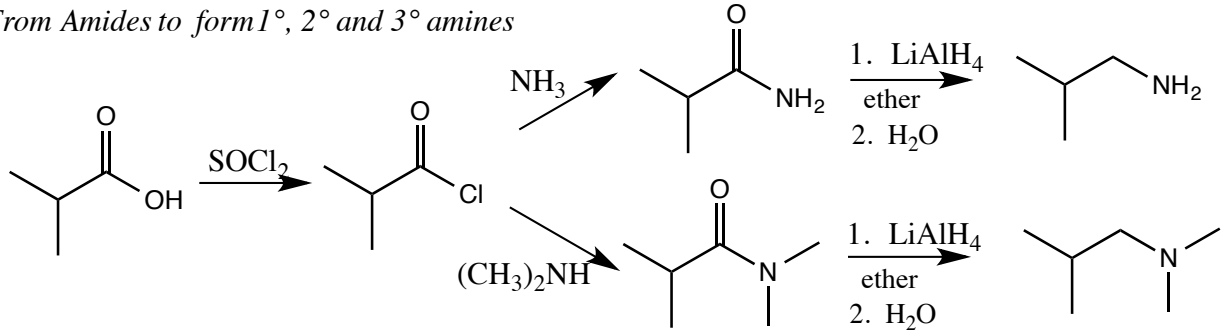


- *anilines are fairly poor bases because their lone pairs are less available for protonation since they are tied up via resonance with the aromatic ring*
- *pyridines are good bases since their lone pair is NOT part of the pi system or engaged in resonance*
- *aromatic amines like pyrrole are poor bases since their lone pairs are part of the pi system required for resonance and are therefore not available for protonation*

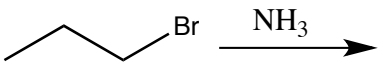
Problems: 2

Synthesis of Amines

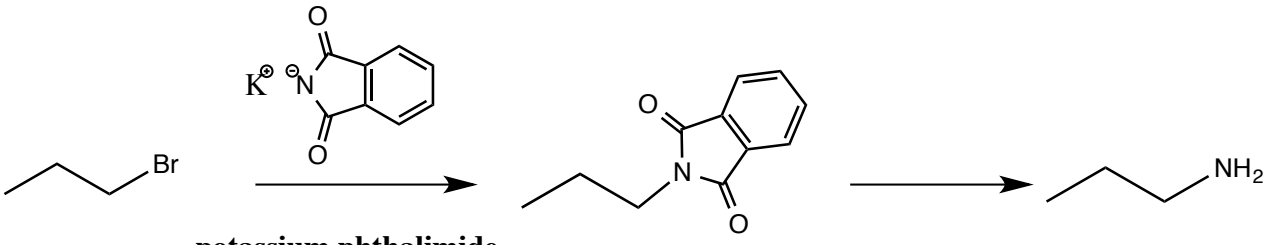
From Amides to form 1°, 2° and 3° amines



Nucleophilic Substitution Reactions to form 1° amines



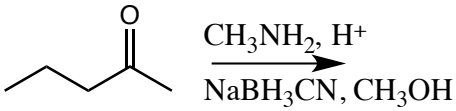
Gabriel Synthesis

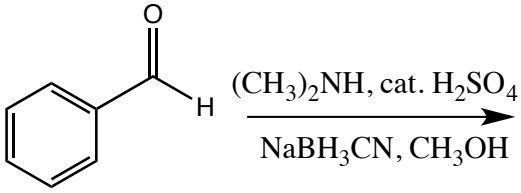


potassium phthalimide

- *simple SN2 reactions of amines with alkyl halides are not often useful methods for the syntheis of amines since over-alkylation often results*
- *the Gabriel synthesis utilizes potassium phthalimide as a nucleophile since it will react only once*
- *hydrolysis of the Gabriel intermediate affords 1° amines in high yields*

Reductive Amination



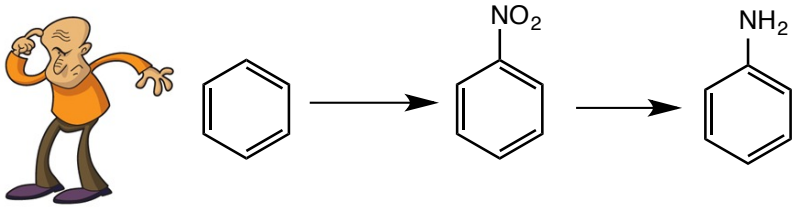


- *reductive amination affords 1°, 2° or 3° amines when a ketone or aldehyde is treated with the appropriate amine*
- *the intermediate in the process is an imine*
- *reduction of the imine takes place using the specialized borohydride reducing agent, sodium cyanoborohydride ($NaBH_3CN$)*

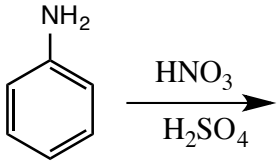
Problems: 3,4

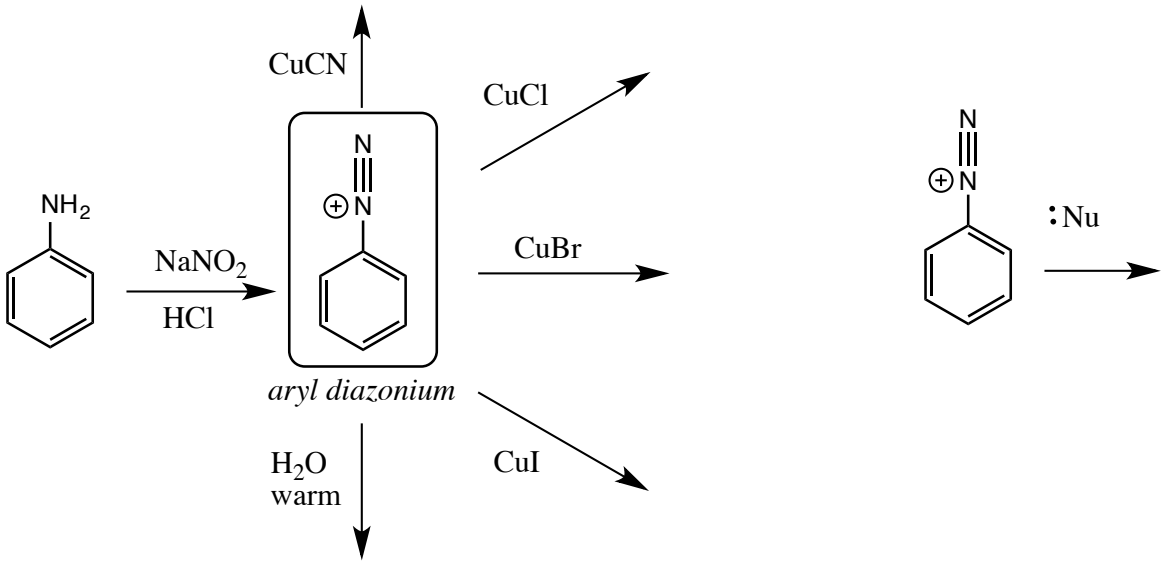
Aniline Reactions

Synthesis of Anilines



Diazotization of Anilines





- *diazotization of aniline occurs when anilines are treated with nitrous acid (HNO_2) generated by mixing HCl with $NaNO_2$ [NOTE: this is different than nitric acid (HNO_3)]*
- *treatment of the aryl diazonium salt with CuX results in a substitution reaction (Sandemeyer Reaction)*
- *warming the aryl diazonium salt in water results in the formation of phenols*