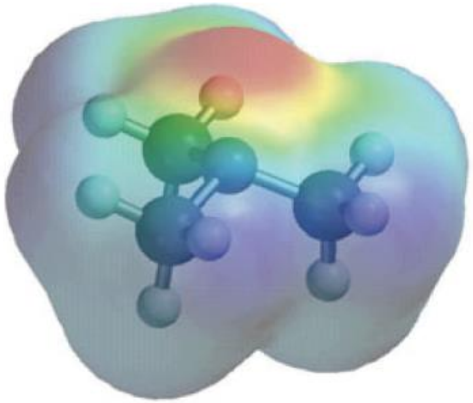
2302106 – Basic Organic Chemistry for ISE – Part II

Lecture 3-2

Amines – Basicity

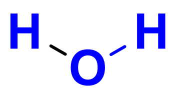


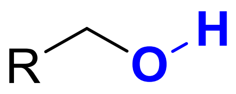
Instructor: Dr. Tanatorn Khotavivattana
E-mail: tanatorn.k@chula.ac.th

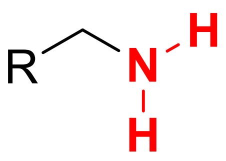
Recommended Textbook:

Chapter 19 in *Organic Chemistry*, 8th Edition, L. G. Wade, Jr., **2010**, Prentice Hall (Pearson Education)

Acidity/Basicity of Water vs Alcohols vs Amines

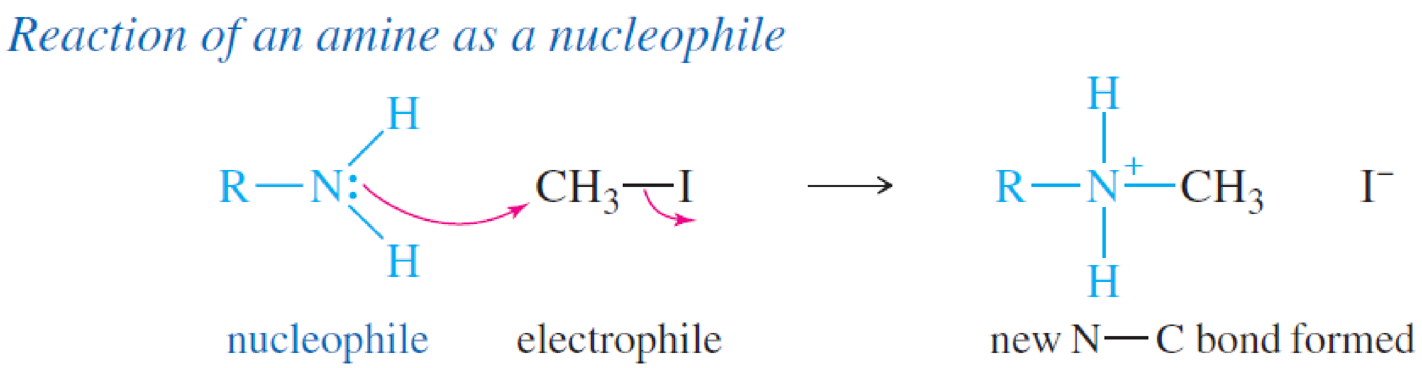




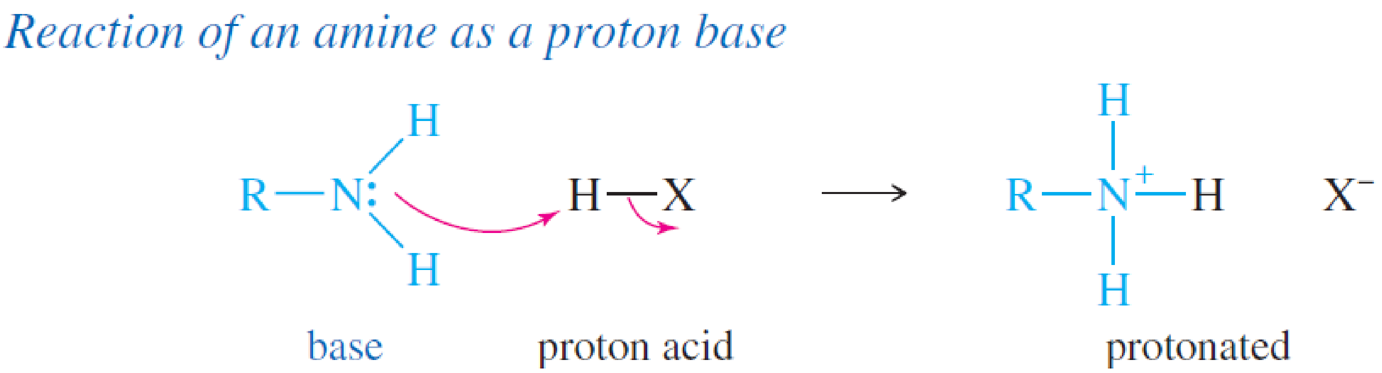


Basicity of Amines

- An amine is a **Nucleophile** (a **Lewis base**) because its lone pair of nonbonding electrons can form a bond with an electrophile



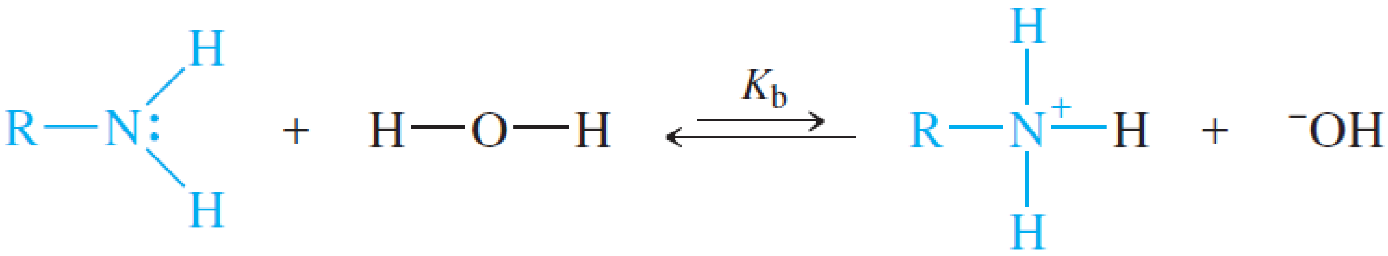
- An amine can also act as a **Brønsted–Lowry base** by accepting a proton from a proton acid



Basicity of Amines

- An amine can abstract a proton from water, giving an ammonium ion and a hydroxide ion

- The equilibrium constant for this reaction is called the **base-dissociation constant** for the amine, symbolized by $\mathbf{K_b}$



$$K_b = \frac{[RNH_3^+][^-OH]}{[RNH_2]} \qquad pK_b = -\log_{10} K_b$$

Stronger bases have smaller values of pK_b.

- Values of K_b for most amines are fairly small (about 10^{-3} or smaller; $pK_b > 3$), and the equilibrium for this dissociation lies toward the left.

Basicity of Nitrogen-Containing Compounds

NH_3

ammonia

$pK_b = 4.74$

CH_3-NH_2

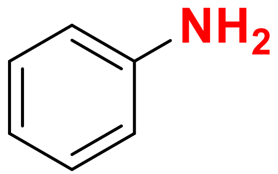
methylamine

$pK_b = 3.36$

CH_3-NH-CH_3

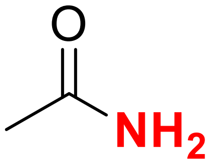
methylamine

$pK_b = 3.28$



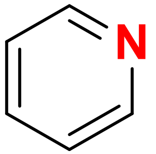
aniline

$pK_b = 9.40$



amide

$pK_b = 14.5$



pyridine

$pK_b = 8.75$

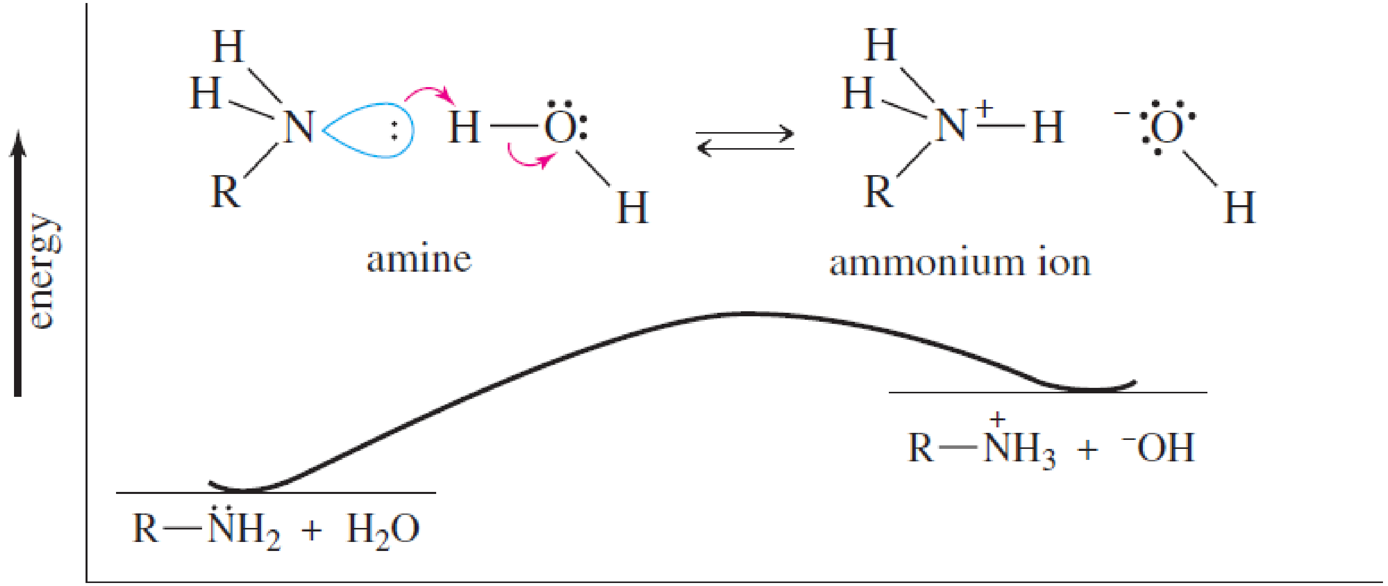
$H_3C-C\equiv N$

nitrile

$pK_b = 24$

Effects on Basicity

Potential-energy diagram of the base dissociation reaction of an amine



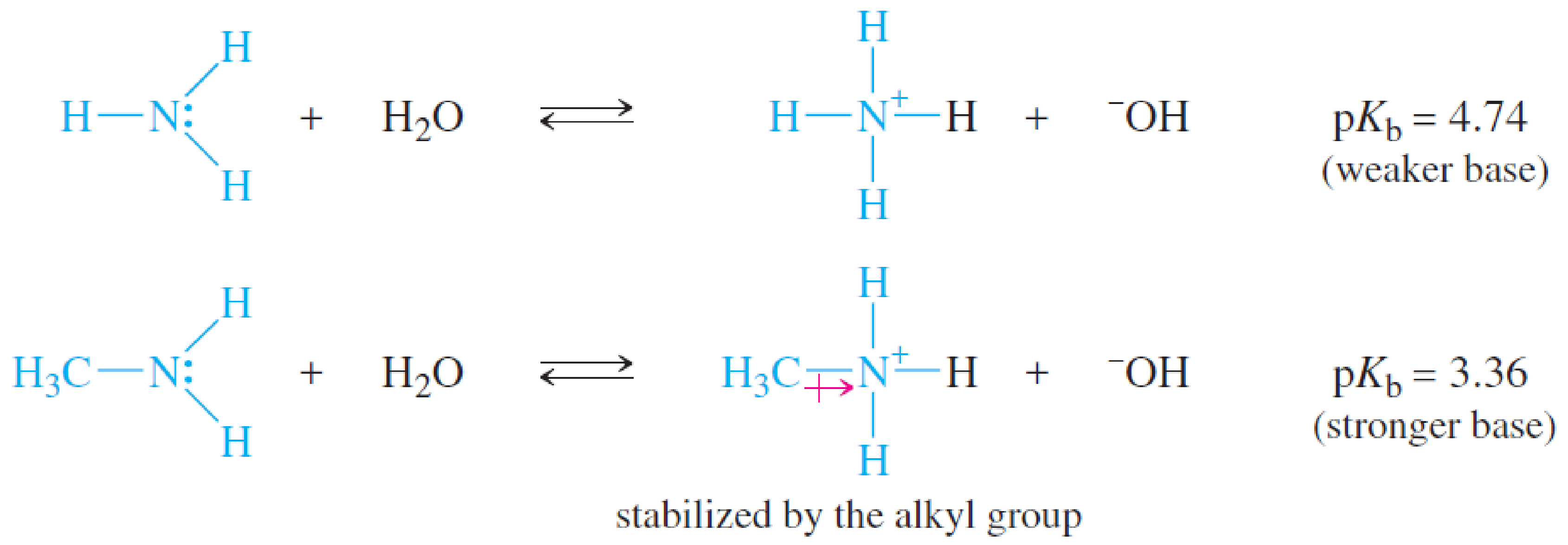
Any structural feature that **stabilises the free amine** shifts the reaction toward the left, making the amine a **weaker base**

Any structural feature that **stabilises the ammonium ion** shifts the reaction toward the right, making the amine a **stronger base**

Effects on Basicity

1) Alkyl Substitution

- Alkyl groups are **electron-donating** toward cations; **stabilise the positive charge** on nitrogen



- This stabilisation lowers the potential energy of the methylammonium cation, making methylamine a **stronger base** than ammonia

1) Alkyl Substitution

Relative basicity in gas phase:

$$(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$$

More alkyl substitution results in more stabilization of the alkylaminium ion

Relative basicity in aqueous solution:

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

Less hydrogen bonding to water – less stabilization of the alkylaminium ion

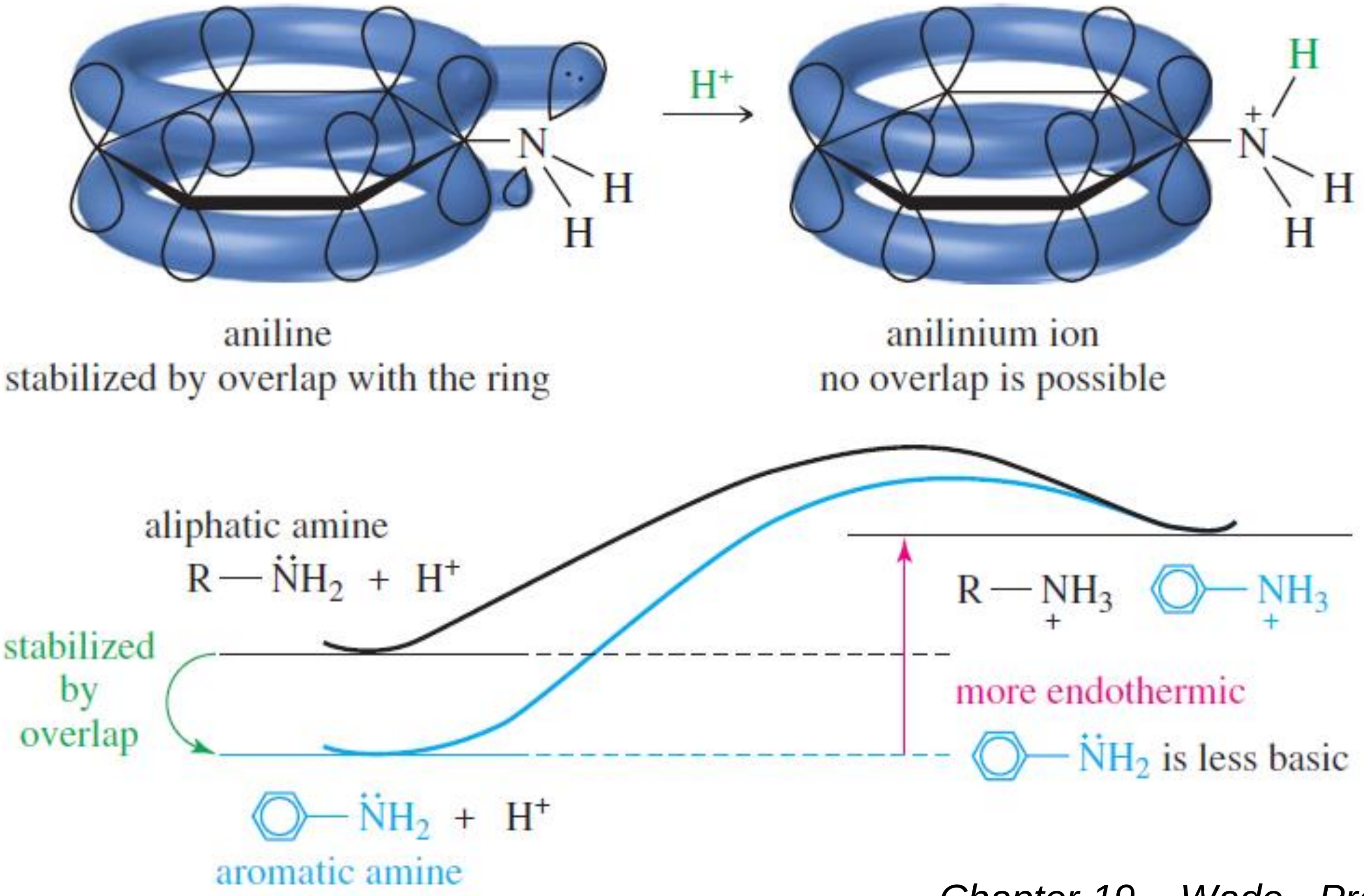
$(CH_3)_3N$ $(CH_3)_2NH$ CH_3NH_2 NH_3

More alkyl substitution results in more stabilization of the alkylaminium ion

Effects on Basicity

2) Resonance effect

- **Arylamines** (anilines and their derivatives) are **much weaker bases** than simple aliphatic amines



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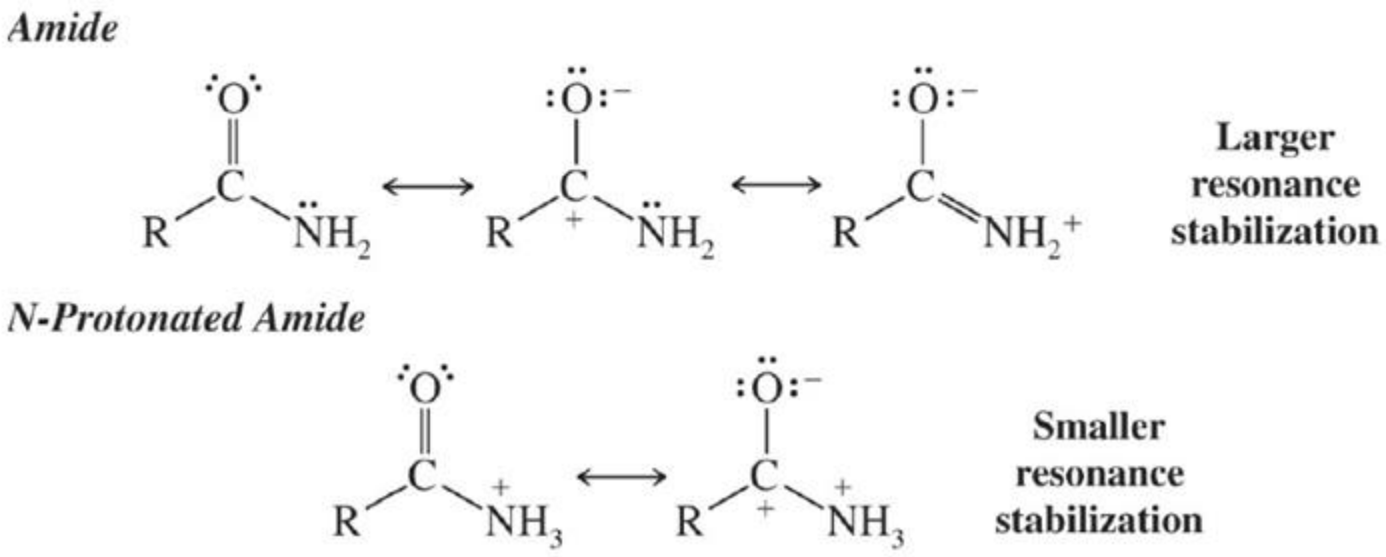
Effects on Basicity

2) Resonance effect

- **Amides** are **much less basic** than simple amines
- Nitrogen lone pair of amide is **delocalised** to the carbonyl oxygen

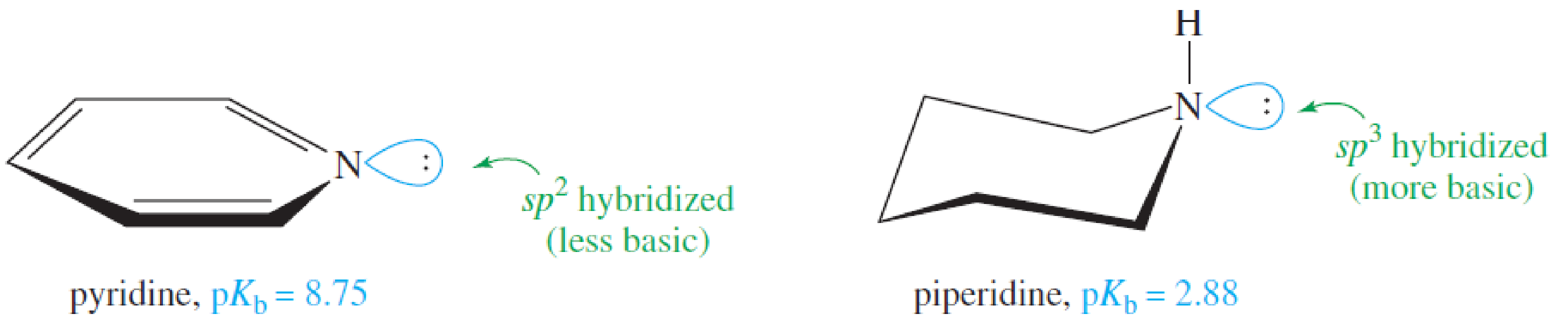


- Amide is greatly **stabilized by resonance** but the protonated amide is not

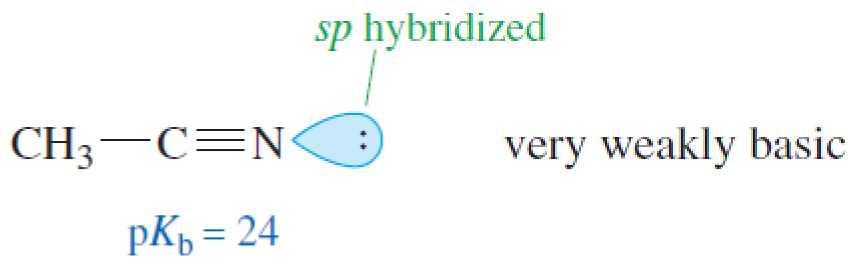
Effects on Basicity

3) Hybridisation effect

- **Unsaturated amines** tend to be weaker bases than simple aliphatic amines

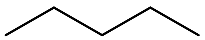


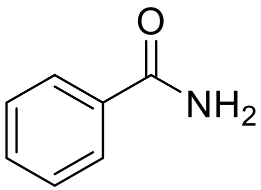
- Electrons are held **more tightly** by orbitals with **more s character**
- Pyridine's nonbonding electrons are **less available** for bonding to a proton
- The effect of is even more pronounced in **nitriles** with **sp hybridization**

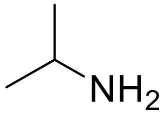


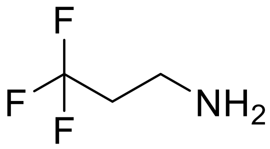
Effects on Basicity - Example

Rank the following compounds in order of increasing basicity









Effects on Basicity - Example

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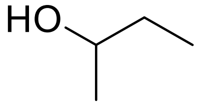
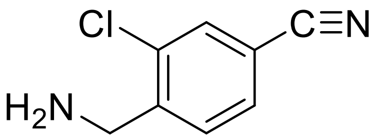
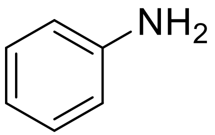
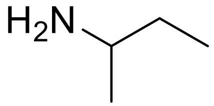


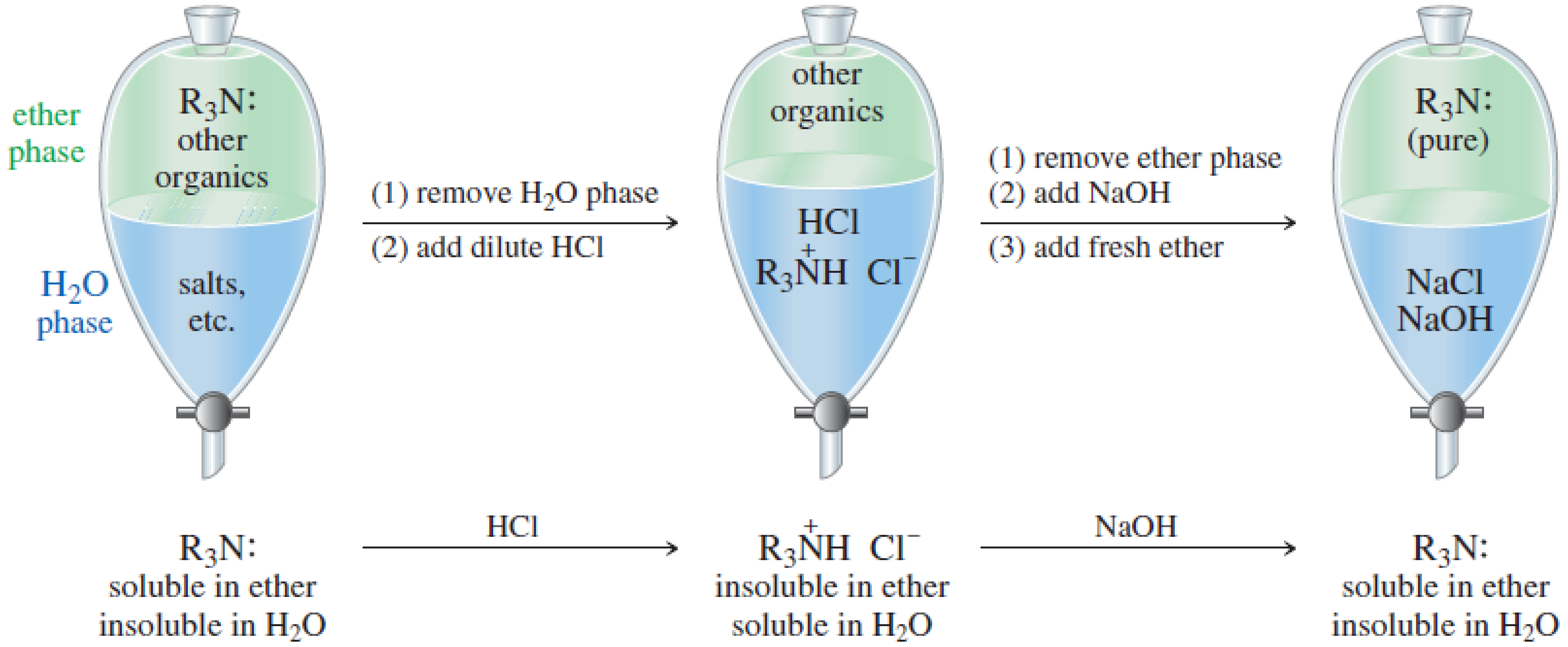






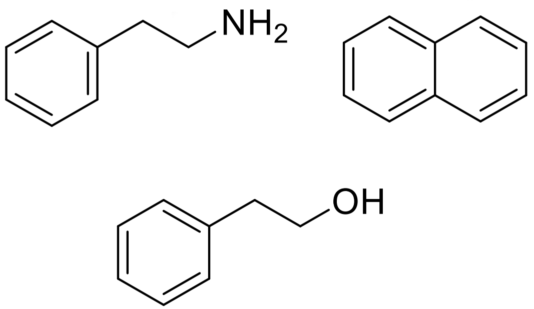
Salts of Amines

- Protonation of an amine gives an **amine salt**
- Amine salts are **ionic**, **high-melting**, **non-volatile solids**. They are much **more soluble in water** than the parent amines, and they are only slightly soluble in nonpolar organic solvents



- Use the formation of amine salts to separate amines from less basic compounds

Acid-Base Extraction Example:



Mixture!