Stability/Reactivity/Selectivity Principles

Key note: The "reactant" or "product" in the following is always **relative to the rate-determiningstep of a reaction mechanism**. So it's always **crucial to know what the mechanism for a reaction is** in order to apply these principles.

- **1.** Reactant Stability/Reactivity: The more stable the reactant, the less reactive it will be. In terms of rates, this means that the more stable the reactant, the slower it will react.
 - Nucleophilicity in Ch. 6 Reactions

• Electrophilicity in Ch. 6 Reactions (Reactivity in S_N2, S_N1, E2, E1 Reactions)

- **2.** <u>Product Stability/Reactivity</u>: The <u>more stable the product</u>, the <u>more favorable its formation</u> will be. In terms of rates, this means that the <u>more stable the product</u>, the faster the reaction. (The concept here is that the more stable the product, the more favorable it will be to make that product.)
 - $S_N 1$, E1 Reactivity in Ch. 6 Reactions:

$$\searrow_{\mathsf{Br}}$$
 < \bigvee_{Br} < \bigvee_{Br} < \bigvee_{Br}

Why: Because of the stability of the cation produced in the rate-determining step

- **3.** Transition-State Stability/Reactivity: The more stable the transition state, the faster the reaction will be. (The concept here is that the lower the transition state, the more easily it will be crossed.)
 - S_N2 Reactivity in Ch. 6 Reactions

$$3^{\circ}$$
 < 2° < 1° Br < 1° plus allylic

Why: Steric congestion in the S_N2 transition-state. In the case of allylic halides, the transition state is stabilized for orbital reasons, not steric reasons.

- **4.** Reactant Stability/Reactivity/Selectivity: The more stable the reactant, the less reactive it will be and the more selective it will be. (For a reaction where the same two reactants can give either of two products.)
 - No examples from Chapter 6
 - From Chapter 4, selectivity in the reaction of bromine versus chlorine with alkanes via radical halogenation