

Problem Set 10

1. Read Chapter 8 Section 1: You should be familiar with the three major types of reactions that organic compounds undergo—namely, addition, elimination and substitution reactions—and should be able to recognize when one of those reactions has occurred based on the structures of the starting material and product in a reaction.
2. Read Chapter 8 Section 2: You are responsible for knowing that the pi bond of alkenes is nucleophilic such that an alkene can donate a pair pi electrons easily to form a bond to electrophiles. Alkenes represent the first functional group you have studied in which carbon can act as a nucleophile. In the presence of electrophilic species (e.g., HX, H₂O, etc.), alkenes undergo electrophilic addition reactions in which the electrophile and nucleophile bonded to the electrophile add across the C=C bond. Addition reactions to alkenes are useful because they can produce a wide variety of different substituted alkanes.
3. Read Chapter 8 Section 3: You are responsible for knowing Electrophilic Addition of Hydrogen Halides to alkenes. What is the mechanism for that class of reactions? You should be familiar with Markovnikov's Rule—that is, that electrophilic addition reactions proceed through a carbocation intermediate such that the electrophile adds to the less substituted carbon to form the most stable carbocation intermediate. Become familiar with the concepts of Markovnikov vs. Anti-Markovnikov products. You should know that Free-Radical Addition of HBr leads to formation of the Anti-Markovnikov product. Why? How does the mechanism of free-radical addition differ from that of electrophilic addition? Study Mechanism 8-2 Ionic Addition of HX to an Alkene and Mechanism 8-3 Free-Radical Addition of HBr to Alkenes. You can recognize when free-radical addition will occur rather than electrophilic addition when a peroxide (ROOR) is used.

Work the following problems found in Section 3 of Chapter 8: **Problems 1-4.**

4. Read Chapter 8 Section 4: You are responsible for knowing that hydration of alkenes via Electrophilic Addition of Water leads to formation of Markovnikov alcohols as the major product. Study Mechanism 8-4 Acid-Catalyzed Hydration of an Alkene. Many alkenes do not undergo acid-catalyzed hydration easily. Those that form 2° carbocation intermediates are prone to undergoing rearrangement via a hydride or alkyl shift if rearrangement gives a more substituted carbocation. Therefore, hydration by oxymercuration-demercuration generally is a better method to prepare Markovnikov alcohols from alkenes.

Work the following problems found in Section 4 of Chapter 8: **Problems 5 and 6.**

5. Read Chapter 8 Sections 5-6: You should be familiar with hydration of alkenes via Oxymercuration-Demercuration and that those reactions produce Markovnikov alcohols as the major product. What is the role of the mercury cation and how does the mechanism for oxymercuration differ from that of acid-catalyzed addition of water (compare mechanisms 8-4 and 8-5)? Oxymercuration reactions proceed via formation of a cyclic mercurinium cation intermediate (a non-classical carbocation) where the mercury ion sits on one face, requiring that nucleophilic water approach from the opposite face. The resulting alcohol necessarily is the product of *anti* addition. Removal of the mercury cation requires a second step involving nucleophilic attack by hydride (H⁻) from NaBH₄. The principle advantage of oxymercuration over acid-catalyzed hydration is that the cyclic mercurinium ion intermediate prevents rearrangement from occurring. Alkoxymercuration-Demercuration, which uses alcohols instead of water, produce Markovnikov ethers as products. Study Mechanism 8-5 Oxymercuration of an Alkene and Mechanism 8-6 Alkoxymercuration of an Alkene.

Work the following problems found in Section 11 of Chapter 8: **Problems 7-9.**

6. Read Chapter 8 Section 7: You should be familiar with hydroboration reactions and understand why hydroboration of alkenes leads to formation of anti-Markovnikov alcohols as the major product. How does the concerted mechanism of hydroboration differ from the normal mechanism of electrophilic addition involving an intermediate? Study mechanism 8-6. How does concerted addition affect the stereochemistry of the product? Why does boron add to the less substituted carbon in the alkene C=C bond? You should be familiar with the borane reagents used for hydroboration—namely, $\text{BH}_3 \cdot \text{THF}$ or B_2H_6 —and why a second reaction involving oxidation with H_2O_2 is required to remove boron and form the alcohol product. You also are responsible for knowing why addition of the H and OH occurs stereospecifically via *syn* addition. Study Mechanism 8-6 Hydroboration of an Alkene.

Work the following problems found in Section 7 of Chapter 8: **Problems 10-16.**

Work the following problems found at the back of Chapter 8: **Problems 46a,c,e,f,n,p, 47a,h,i,l, 49e,f, 51a,b,c,e, 56a,b,c,e, 57, 59, 66, and 67.**