

Problem Set 9

1. Read Chapter 7 Section 9: You are responsible for knowing that alkenes can be formed via dehydrohalogenation reactions. Alkyl halides undergo elimination of a proton and a halide anion in the presence of a base. Nucleophiles that are the conjugate bases of weak acids can act both as nucleophiles and as bases. Neutral nucleophiles such as water, alcohols, and amines also can act as bases. Therefore, dehydrohalogenation reactions (elimination reactions) almost always compete with substitution reactions.
2. Read Chapter 7 Section 10: You should be familiar with the E1 reaction (1st-order elimination), the general mechanism, and that E1 reactions compete with S_N1 reactions. Why does formation of a carbocation intermediate lead to products both of substitution and elimination? Study Key Mechanism 7-1: The E1 Reaction. You should be able to explain why a carbocation is able to undergo elimination in the absence of a strong base. Be aware that rearrangement via a hydride (H:) or alkyl (R:) shift may occur in elimination reactions that proceed through an E1 mechanism. Rearrangement generally occurs only if a 1° or 2° carbocation is formed that can form a more substituted carbocation via rearrangement. Study Mechanism 7-2 Rearrangement in an E1 Reaction and also section 6-15 in chapter 6.

Work the following problems found in Section 10 of Chapter 7: **Problems 16-20.**

3. Read Chapter 7 Section 11: You are responsible for knowing Zaitsev's Rule—namely, that more substituted alkenes usually predominate in elimination reactions because they are more stable (lower in energy) than less substituted alkenes. Review Section 7-8 on the Stability of Alkenes in Chapter 7.

Work the following problem found in Section 11 of Chapter 7: **Problems 21 and 22.**

4. Read Chapter 6 Section 12: You should be familiar with the E2 reaction (2nd-order elimination), the general mechanism, and that E2 reactions compete with S_N2 reactions when the nucleophile is a strong base or a large, sterically-hindered base/nucleophile. How do you know when a nucleophile is a strong base? Can you recognize when a nucleophile is likely to promote E2 elimination? Study Key Mechanism 7-3 The E2 Reaction. You should know the order of reactivity of alkyl halides (3° > 2° > 1°—why?) and that E2 reactions often generate mixtures of alkene products that favor more substituted alkenes according to Zaitsev's Rule.

Work the following problems found in Section 12 of Chapter 7: **Problems 23 and 24.**

5. Read Chapter 7 Section 13: You should know that using sterically bulky bases (e.g., *t*-butoxide, isopropoxide, etc.) to carry out dehydrohalogenation in E2 reactions can lead to formation of less-substituted alkenes (Hofmann products) that do not follow Zaitsev's rule. Hofmann alkenes may form if steric hindrance prevents a bulky base from abstracting a proton that is sterically hindered. Abstraction of a less sterically hindered proton often produces alkenes that are the least-highly substituted product.

Work the following problem found in Section 13 of Chapter 7: **Problem 25.**

6. Read Chapter 7 Section 14: You are responsible for knowing that E2 reactions are stereospecific because the alkyl halide must be in the *anti*-coplanar conformation (lower energy) or *syn*-coplanar conformation (higher energy) for elimination to occur. It helps to make a molecular model and/or Newman projection viewing down the bond of the two carbon atoms bearing the halogen and the adjacent hydrogen atom to determine (1) if the alkyl halide can achieve a conformation where the

halogen and hydrogen are *anti*-coplanar, and (2) what the stereochemistry of the product is—*cis/trans* or *E/Z*—by examining the relative positions of the substituents on those two carbon atoms. Study Mechanism 7-4: Stereochemistry of the E2 Reaction and Figure 7-10 showing alignment of the hybridized orbitals in the *anti*-coplanar and *syn*-coplanar arrangements.

Work the following problems found in Section 14 of Chapter 7: **Problems 26 and 27.**

7. Read Chapter 7 Section 15: This section discusses E2 reactions with substituted cyclohexanes and the impact of chair conformations on reactivity. Given that dehydrohalogenation requires H and X to be *anti*-coplanar, E2 elimination can only take place when H and X reside in a *trans*-diaxial arrangement on adjacent carbon atoms in the ring. It helps to examine a molecular model or Newman projection viewing down the bond bearing the H and X atoms to determine if a *trans*-diaxial arrangement is possible in one of the two ring-flip chair conformations. Elimination will not occur if a *trans*-diaxial arrangement is not possible.

Work the following problems found in Section 5 of Chapter 7: **Problems 28-31.**

8. Read Chapter 7 Section 16: You are responsible for knowing the difference between E1 and E2 reactions, when to expect those reactions to occur, and why nucleophiles that are strong bases or sterically hindered bases/nucleophiles promote E2 reactions. Why do some nucleophiles favor elimination over substitution, while others favor substitution over elimination? How does the degree of substitution on the substrate affect the relative rates of reactivity of alkyl halides toward E1 and E2 reactions?

Work the following problem found in Section 16 of Chapter 7: **Problem 32.**

9. Read Chapter 7 Section 17: This section discusses competition between substitution and elimination reactions. Study Summary Table: Substitution and Elimination Reactions of Alkyl Halides and also Problem-Solving Strategy Prediction Substitutions and Eliminations.

Work the following problem found in Section 17 of Chapter 7: **Problem 33.**

10. Read Chapter 7 Section 18: You are responsible for knowing that alcohols can be converted into alkenes by removing water (dehydration) to form a C=C bond, and how the mechanism of acid-catalyzed dehydration works. What specific role does the acid catalyst play? You should know that it is important to use strong acids such as H₂SO₄ and H₃PO₄ as the catalyst because the corresponding conjugate bases of those acids do not act as nucleophiles. What might happen if an acid such as HCl, HBr, or HI were used as the catalyst? Study Key Mechanism 7-5 Acid-Catalyzed Dehydration of an Alcohol.

Work the following problems found in Section 18 of Chapter 7: **Problems 34 and 35.**

11. Read Chapter 7 Section 19: This section describes how alkanes are converted into alkenes by elimination of hydrogen (H₂) in the presence of a transition metal catalyst. These reactions are used widely in industry to prepare alkenes from alkanes isolated from petroleum. Dehydrogenation by this method generally is not used on a small scale in research labs because the reaction is non-selective and produces mixtures of alkenes.
12. Read the Problem-Solving Strategy Proposing Reaction Mechanisms at the end of Chapter 7, which describes the general principles involved in proposing and drawing reaction mechanisms. Proposing

reaction mechanisms is one of most important tools a chemist has in order to explain how chemical reactions work. It is essential that you work toward mastering reaction mechanisms if you are planning a career in the chemical sciences.

Work the following problems found at the end of Chapter 7: **Problems 37-39.**

Work the following problems found at the back of Chapter 7: **Problems 48-62, 64, 65, 68, 69, 71-73.**